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POTASSIUM-BEARING MINERALS AS A SOURCE OF POTASSIUM FOR PLANT GROWTH

ERNEST DE TURK

University of Illinois

Received for publication October 2, 1919

I. INTRODUCTION

The necessity of using potassium fertilizers in general agricultural practice is not so vital as the public has been led to believe. The fact that applications of potassium salts have caused increases in crop yields at many of the experiment stations of the United States, together with the propaganda work of the German Kali Syndicate, has led to the popular belief that potassium fertilization is essential for the most profitable crop production on most of our common agricultural soils. As a matter of fact, the majority of soils in the United States contain from 20,000 to more than 60,000 pounds (24) of potassium per acre—$6\frac{2}{3}$ inches (2,000,000 lbs.). While most of this is held in the relatively insoluble form of complex silicates, crop yields as a rule are not limited by deficiencies of available potassium. Furthermore, it is not probable that potassium would become a limiting element under soil treatments that would otherwise produce maximum yields, because those same treatments, such as returning organic manures, improving the physical condition of the soil, and the addition of the usual limiting elements, nitrogen and phosphorus, will tend toward the maintenance of an increasing amount of readily available potassium by the return of this element in residues and manure, by bringing about increased solution of mineral potassium and by increasing the root systems and hence the feeding power of the crops grown. The earth's crust, to a depth of ten miles, has been estimated to contan an average of 2.32 per cent of potassium (66). More recent calculations place the estimate at 2.46 per cent (33, p. 13). This indicates that the problem of potassium for agriculture is ultimately one of liberation rather than of supply for normal agricultural soils and the common farm crops.

Experiments at the Pennsylvania (33, p. 423, 428–431; 36), Ohio (33, p. 442), Illinois (33, p. 466; 34, 35) and other experiment stations indicate that potassium salts are applied, either alone or with other fertilizers, at a loss as a rule, and at best at a very small profit in a few instances.

While the above statements are true for the majority of our farm lands, there are quite large areas in Illinois and other states which are markedly deficient in potassium. These consist mainly of muck and deep peat soils, and light

sandy soils. They contain from practically no potassium to 4000 pounds of potassium per acre—6⅔ inches. In the case of the sandy soils some are actually deficient in total potassium, while others, which respond equally well to potassium fertilization, contain considerable amounts of the element, but the most of it is contained in the coarser particles. Because of the relatively small surface of the sand particles, their potassium can not become available to plants to any appreciable extent. A sample of dune sand, representative of considerable areas in Illinois, was analyzed by the writer. Of the 20,600 pounds of potassium per 2,000,000 pounds which it contained, 94.93 per cent was contained in the combined sands and 5.10 per cent in the silt and clay combined.

On these peaty and sandy soils the use of potassium salts has proved quite profitable, and is in fact absolutely necessary to successful crop production on much of the peat soil. The prohibitive price of potassium fertilizers and their entire withdrawal from the market during the last four or five years has interfered seriously with the profitable cropping of these potassium-poor soils. Soluble potassium salts from any of the several American sources are too high-priced for agricultural use. Potassium-bearing minerals are very abundant in the United States, and are already being produced in commercial quantities in several states for other than agricultural purposes.

Potassium feldspars, orthoclase and microcline ($KAlSi_3O_8$) are extremely abundant throughout the United States. Deposits have been extensively developed, however, only in California and some of the eastern states, particularly Maine, Connecticut, Pennsylvania, New York and Maryland (15, 39). The average potassium content is 7 to 11 per cent and the average price per ton in 1914 was $8.31; in 1915, $8.33 and in 1916, $9.30 (15).

The Leucite Hills in Sweetwater County, Wyoming, are the principal source of leucite ($KAlSi_2O_6$) in the United States. The area has been carefully studied and mapped by Schultz and Cross (57) who estimate the minimum amount of commercially available potassium at 164,000,000 tons. The scarcity of leucite among igneous rocks is due to the fact that it is formed from the molten magma only when there is a deficiency of silica. Whenever sufficient silica is present orthoclase, which contains 50 per cent more molecules of SiO_2 than leucite, is formed (57, p. 13).

> Alunite is a hydrated basic sulfate of potassium and aluminum ($K_2O.3Al_2O_3.4SO_3.6H_2O$). . . . . It is usually contaminated with silica and other impurities and often has a part of its potash replaced by soda. It is widely disseminated through porphyritic volcanic rocks as an alteration product of feldspars, but it usually occurs in such small quantity or is contaminated with so much gangue material that it has no commercial value (26, p. 429).

High-grade alunite is limited in its distribution mainly to certain sections of Utah, Nevada and Colorado. The deposits are easily worked, being near the surface, and according to estimates by Loughlin (45), contain enough recoverable potassium to supply a large part of the American demand. The

ease with which the potassium is completely extracted from alunite as the sulfate (ignition to 750°C. followed by leaching with water) will probably lead to its use almost exclusively for the production of commercial potassium sulfate.

Muscovite ($KH_2Al_3Si_3O_{12}$) is quite abundant in many parts of the United States and is produced commercially, principally as sheet mica, in twelve states. North Carolina produced in 1916, 63 per cent of the total output of the country; New Hampshire, 14 per cent and South Dakota 13 per cent. Scrap mica, being the clippings from the sheet mica trimming plants, is used, ground, in a number of industries and could be obtained for agricultural use should it prove profitable. The price of scrap mica up to 1913, for the 3000 to 4000 tons produced annually, was $11 to $13 a ton, and in 1916, $16 a ton (55).

Lepidolite is a complex micaceous silicate, in which part of the potassium is replaced by lithium. It is usually a mixture of the pure mineral and mica, and contains 8 to 9 per cent of potassium. It is produced in California, Maine and the Black Hills of South Dakota. It is used mainly as a source of lithium for the preparation of lithium salts, and probably would not be commercially available in large amounts for agricultural purposes. The present cost is $15 to $20 a ton (56).

The great drawback to the use of potassium minerals as fertilizers is their low solubility, and hence, comparative unavailability to plants. There have been many attempts to extract soluble potassium salts from minerals by various treatments, and also to subject the minerals to processes which would render the potassium readily available to plants, so that the treated minerals could be used directly upon the soil, thus avoiding the expensive processes of extraction and evaporation. The extent of these efforts is indicated by the fact that the United States Patent Office granted 128 patents for processes of treating silicate rocks for the extraction of potassium between 1904 and 1917 (26). It would seem that the difficulty of the low availability to plants of mineral potassium might be greatly lessened on peat soil, where the decomposition of the large amount of organic matter present, even though slow, should hasten the decomposition of the minerals.

The object of the experiments to be reported in this paper was (a) to determine to what extent the potassium in certain minerals will become available when mixed with peat soil, using both the growth of a crop and chemical analysis as a measure of the amount of soluble potassium, and (b) to determine the effect of certain more active organic materials and soluble salts upon the solubility of the potassium in those minerals.

II. REVIEW OF PREVIOUS INVESTIGATIONS

A complete review of all the work which has been done concerning the rendering available of soil potassium would obviously be outside the scope of this work. The idea of using powdered minerals, or "stone-meal" as a source of potassium is not new.

In 1848 Magnus (46) grew a barley crop to maturity, and obtained well matured grain in an artificial soil in which powdered feldspar was the sole source of potassium. Since then numerous experiments have been carried out in which the results recorded are more or less contradictory in regard to the potassium absorbed by the plants. The variations are no doubt due to the conditions of the experiments and in a still greater degree to the kinds of minerals, their source and stage of weathering.

Missoux in 1853 (48) noted the beneficial effect upon plant growth of waste rock dust from granite quarries.

H. Hoffman, 1861–1863 (32) conducted wheat culture tests for two years on plats 9 by 50 feet, using ground nephelin-dolerite containing 4.98 per cent of potassium and considerable amounts of calcium, magnesium and phosphorus. The crops on the fertilized plats had a much better appearance during June of each season, but the harvest showed larger yields of grain from the unfertilized plats.

During the next twenty years little was done with silicate minerals as fertilizers, though a great deal of work was reported dealing with their chemical decomposition and the nature of their weathering products.

In 1887 Aitken (1,1a) in Scotland grew peas and turnips on $\frac{1}{40}$-acre field plat treated with potassium sulfate and 120-mesh feldspar in comparison. The following yields were obtained from the treatments indicated:

TREATMENT	YIELD OF PEAS	YIELD OF TURNIPS
	pounds	*pounds*
No potassium	96	476
K_2SO_4, 3 pounds	114	482
Feldspar, 12 pounds	102	496

While the feldspar here produced results for peas almost equal to the soluble potassium salt, and a greater yield for turnips, the small percentage increases of both over the yields of the untreated checks, indicate that the soil was not particularly deficient in potassium. Furthermore, the work at the Rothamsted Station indicates that turnips do not respond readily to potassium fertilization. The average turnip yields on the Agdell field were increased by over 13,000 pounds by the use of phosphorus, while a further addition of mineral fertilizers consisting of sodium, potassium and magnesium salts produced no further increase (33, p. 346). On the Barn field, phosphorus and potassium produced no greater increases than phosphorus alone (33, p. 399).

Nilson (50) grew oats on a peat soil in Sweden, comparing feldspar with potassium sulfate, applying 2.5 to 4 times as much potassium in the feldspar as in the soluble salt. Phosphorus and nitrogen were supplied, the latter as crude Chile saltpeter. The yields were as follows, from plats of 100 plants each:

TREATMENT	YIELD OF OATS
	gm.
Nothing	17.3
P + K_2SO_4	394.1
P + Feldspar	328.0
P + N	439.5
P + N + K_2SO_4	603.5
P + N + Feldspar	463.7

These results indicate large increases where feldspar was used and still larger for K_2SO_4, but the experiment does not prove definitely that the increase is caused by the potassium in the mineral. The large yield from phosphorus and nitrogen would indicate either that the soil was not deficient in available potassium, or that potassium was being added in the fertilizer, probably as an impurity in the Chile saltpeter. The high yields from all the plats receiving phosphorus, together with the absence of a plat receiving phosphorus alone, suggests that phosphorus may be the limiting element in that soil and for that crop.

In 1889 Feilitzen (20, 21) grew crops on peat soils, and peat mixed with sand in sunken zinc cylinders, comparing feldspar with kainit as a source of potassium. With oats, equal yields were obtained with feldspar and kainit, but in later experiments, with clover, potatoes and peas, the feldspar jars produced no greater yields than where no feldspar was used. These results as a whole are decidedly unfavorable to the feldspar.

In the same year Ballentine (3) at the Maine Experiment Station reported results of pot experiments with feldspar, in which oats was grown in pure quartz sand. The relative yields from KCl, feldspar and no potassium were 100, 79 and 0, respectively. The author's conclusion was that oats could obtain sufficient potassium from the feldspar used to produce a heavy crop of grain, though the feldspar was inferior to soluble potassium salts.

Headden (29) grew oats to maturity in pure quartz sand and feldspar mixed, the plant-food elements other than potassium being supplied in available form. The feldspar was crushed to 1 mm. and included all the fine material. The crop removed 1.20 gm. K per jar in addition to that contained in the seeds. No comparison was made with other forms of potassium.

The earlier work (1901–1903) of Prianischnikov (52), in which crops of tobacco, buckwheat, flax, peas and millet were grown in acid-washed sand, indicated no benefit from orthoclase and but small benefit from mica. The use of ammonium salts as a source of nitrogen produced much smaller yields than sodium nitrate. The ammonium salts either "exerted no solvent action upon the potassium, or any benefit from such solution was overbalanced by the deleterious effect of acidity produced by the nitrification of the ammonium salts." Somewhat later the same investigator (53) carried out very carefully a series of well-planned experiments upon the sand and peat soils of northern

Russia. The object of the first of these was to determine whether plants can obtain potassium only from secondary minerals in the soil, roughly classed as zeolites, or also from the unweathered primary minerals. Nephelin rock, characterized by easy weathering and a tendency to form zeolites, and containing some zeolites was compared with muscovite and orthoclase in acid-washed sand. Hellriegel's nutrient solution, minus potassium, was supplied to all the jars. The results are reproduced in full:

Yields

	KCl	NEPHELIN	MUSCOVITE	ORTHOCLASE	NO K
	gm.	*gm.*	*gm.*	*gm.*	*gm.*
Mustard	13.95	12.68	11.20	5.88	2.77
Buckwheat	10.10	14.30	10.90	2.80	4.40
Millet	6.90	9.70	7.60	4.40	4.70

Percentage utilization of the potassium supplied in the mineral

	NEPHELIN	MUSCOVITE
	per cent	*per cent*
Mustard	25	22
Buckwheat	38	30
Millet	23	17

Orthoclase here seems to be practically worthless while both nephelin and muscovite are approximately equal to soluble potassium in crop-producing power. The amount of potassium which these last two minerals give up to the crop is exceptionally large. A second experiment involved the use of ten different minerals with five crops. Samples of the minerals were also extracted by shaking with 10 per cent solutions of ammonium chloride and of barium chloride, both with and without boiling. The relative amounts of potassium obtained by these extractions were in harmony with the results of the plant culture experiments. The minerals used were finally classified as a result of these experiments into the following three groups, arranged in order of decreasing availability of the potassium:

1. Nephelin.
   Micas, especially biotite.
2. Phillipsite (a zeolite).
   Muscovite.
3. Eläolith,
   Leucite,
   Apophyllite,
   Sanidin,
   Orthoclase,
   Microcline.

Wotschal (69) reported mica superior to the feldspars.

The investigations of Cushman (15) are not conclusive, because the soils used in greenhouse work as well as in cooperative field tests by farmers, were probably not deficient in potassium, most of them having been heavily "potashed" for tobacco the previous years. In these tests, however, the yields of tobacco were the same whether potassium was supplied in feldspar or in potassium carbonate.

Hartwell and Pember (28) secured increases in yields of wheat and millet of 4 to 18 per cent for feldspar as compared with 130 to 248 per cent increases for potassium sulfate. The soil used had been cropped several years with liberal applications of the other plant-food elements, but no potassium. Fifteen pounds of soil were used in each jar.

Skinner and Jackson (58) increased crop yields by 10 to 20 per cent by applications of raw alunite. The same amounts (25 to 500 pounds K_2O per acre) of potassium supplied in ignited alunite produced increases of 35 to 43 per cent.

It is a well-known fact that the calcium and sodium feldspars are much more easily weathered than those of potassium. In the sodium-potassium feldspars, the rapidity of weathering should therefore increase with the proportion of sodium present. In 1913 Blanck (8) reported results of an investigation of the availability of the potassium of a series of feldspars decreasing progressively in potassium content, and increasing in sodium. The minerals were applied so that all jars received equal amounts of potassium, and, consequently, increasing amounts of sodium. Crop yields were increased progressively, in accordance with the hypothesis. This led the investigator to suspect that sodium was replacing potassium in its function in the plant. Analysis of the crops, however, proved that the increases in yields were due to potassium. Following is a summary of the results:

	K IN MINERAL	Na IN MINERAL	MINERAL PER JAR	RATIO Na:K IN JAR	YIELD OF OATS	UTILIZATION OF ELEMENT ADDED	
						K	Na
	per cent	*per cent*	*gm.*		*gm.*	*per cent*	*per cent*
No K					50.6		
Microcline	9.47	1.89	14.13	1:5	52.2	1.12	0.13
Orthoclase	5.72	2.04	23.40	1:3	53.1	2.23	
Oligoclase	0.58	5.47	230.30	10:1	58.7	3.50	
Labradorite	0.38	3.49	350.40	10:1	60.3	3.45	
Albite	0.11	6.19	620.00*	60:1	61.2	7.07	0.46
K_2SO_4					94.5	70.81	

* One-half as much K as in other applications.

A difficulty in the practical use of the low-potassium feldspars is the obvious impossibility of using the large applications necessary to secure the requisite amount of potassium.

Chirikov (12) found in culture experiments that nepheline, biotite and muscovite were good sources of potassium for plants, but not orthoclase. The ineffectiveness of ammonium salts was also shown.

Miller and Van Natta (47) carried out culture experiments in a mixture of river sand and silt loam in the proportion of 8 : 1. Amounts of feldspar were used ranging from 5700 to 23,000 pounds per acre, and compared to 400 pounds per acre of potassium chloride and sulfate. The cultures were grown in 3-gallon jars, and the yields obtained were 10.2 to 12.6 gm. of barley per jar with the feldspar, 11.7 gm. with KCl and 15.7 gm. with K_2SO_4. These results are quite favorable to the feldspar. Larger applications prevented germination of the seeds.

Brooks and Gaskill (9) report some results of individual seasons' crops in which feldspar compared favorably with kainit in long continued field plat experiments at the Massachusetts Experiment Station, but state that as an average of 21 years' continuous use of feldspar, no decided increases have been obtained. The soil on which these investigations were conducted is probably well supplied with total potassium.

In addition to plant culture experiments, many investigations have been carried out to study the effects of various chemical compounds upon the solubility of the potassium of silicate minerals, some of which will be discussed later.

III. SOME CONSIDERATIONS OF THE NATURE AND SIGNIFICANCE OF THE SILICATE MINERALS

Formation, composition and structure

The silicate minerals are complex compounds, usually considered as salts of the polybasic silicic acids. The more common bases involved are sodium, potassium, calcium, magnesium, aluminum and iron. They are as a class highly insoluble in water. Considered from the standpoint of the molecular proportions of bases and silica, they range from strongly basic to strongly acidic compounds. The proportion of base to acid in the various crystallized minerals depends, of course, upon the proportions in the molten mass in which the crystallization took place.

Primary minerals are to be found quite abundantly in metamorphosed and sedimentary rocks as well as in igneous rocks. Here crystallization has occurred, not in a molten mass, but probably in most cases under the influence of superheated steam at high pressure. The researches of Friedel and Sarasin (25), Daubreé (17), Kuhlmann (41) and others show that many silicate and other minerals may be formed artificially by crystallization in the presence of steam and other gases under pressure. The crystallization occurs at a temperature far below the melting point of the minerals after they are once formed.

The close chemical relationship between carbon and silicon early led to the assumption that the silicates must be similar in structure to organic carbon compounds. The classical investigations of Lemberg (43, 43a), however, indicate quite clearly that no such analogy exists. It is a noteworthy fact that certain bases are usually associated in the silicate minerals, while certain others are seldom or never found together. Thus sodium-calcium feldspars are quite common, as are also potassium-magnesium silicates, while on the other hand calcium and potassium are seldom found together, and sodium-magnesium minerals are practically unknown. Lemberg found in studying the alterations of these minerals that there is a decided antipathy between certain bases, as a result of which it is extremely difficult to induce a combination of such bases as sodium and magnesium, for example. Potassium and sodium combine indifferently in the silicate molecule, but to such an extent that sodium-potassium silicates are of fairly common occurrence. These may be merely mixtures of complex sodium silicates and potassium silicates in many cases.

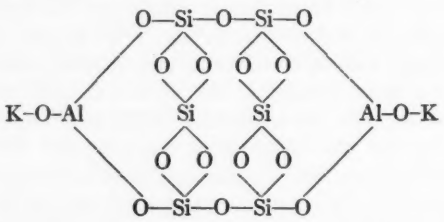
The determination of the structure of silicates is very difficult if not impossible, because they do not possess those properties by the use of which molecular weights are ascertained. The structure is therefore not definitely known in many cases. Cameron and Bell (10) suggest four viewpoints from which these minerals may be considered.

1. They may be considered as combinations of the oxides. Orthoclase, for instance would be $K_2O.Al_2O_3.6SiO_2$. This method of writing the formula, however, gives no clue to the structure of the molecule.

2. They may be molecular compounds, as the alums. But this will not hold for the solution phase; in the solution are found only the simple salts of the various bases.

3. One may consider them double salts of a complex acid, the Si atoms being united through oxygen. Thus orthoclase is a double potassium-aluminum salt of the acid, $H_4Si_3O_8$, or $K_2Al_2(Si_3O_8)_2$,

4. Aluminum may be negative, orthoclase being the potassium salt of $H.AlSi_3O_8$ or $K_2.(AlSi_3O_8)_2$,



These last two views seem the most reasonable, and the last is preferable in view of the amphoteric nature of aluminum and the formation of the alkali hydroxide as the principal soluble hydrolysis product of the alkali aluminosilicates.

Chemical properties

Reaction with water. The solubility of the complex silicates in water is very low. Stoddart (60) states, for instance, that orthoclase is soluble in 37,000 parts of water, and in 4,000 parts of carbonated water. As early as 1848 W. B. and R. E. Rogers (54) studied the solubility of fifty-eight different minerals in water and in carbonated water. Among these were sodium, lithium and potassium feldspars, micas and leucite. In most cases the solubility was great enough to give good qualitative tests for the bases, and the solubility was greater, as a rule, in water containing CO_2 than in pure water. Simple solution of these minerals in water has never been obtained. Being salts of a very weak acid and very strong bases, solution is always accompanied by hydrolytic decomposition. This reaction is usually arrested almost immediately by the gelatinous coating of colloidal silicic acid on the mineral particles, which prevents further action of the solvent. Clarke (13) found that water reacts immediately with rock powders, producing in most cases a reaction alkaline to phenolphthalein, and Cushman (14) states that equilibrium between the rock powder and water is reached in a very few minutes on shaking the two together. This is obviously not a true chemical equilibrium between solid and solvent, but merely the cessation of reaction due to the interference of the colloidal material on the particles. Daubrée in 1867 (18) overcame the interference of the colloidal material by revolving an iron cylinder containing water and pieces of feldspar and quartz. The sliding motion of the fragments kept fresh surfaces exposed so that the decomposing action of the water was progressive. The solution became alkaline and a fine mud (kaolin) was formed as well as considerable soluble and colloidal material and $FeCO_3$. In 8 days he obtained 12.6 gm. of soluble K_2O from 3000 gm. of feldspar in 5 liters of water. The soluble K_2O he reported present mainly as K_2SiO_3. More recently (1905) Cushman (14) obtained similar results by grinding together

powdered feldspar (also powdered glass) and water made up to a thick paste, in a heavy ball mill. By subsequent washing on a filter paper with water, much more sodium and potassium were dissolved out than where the mineral had been ground dry and shaken with water. He assumed that these bases were present as the simple silicates, since the solution obtained was of a glue-like character. In view of the work of Kahlenberg and Lincoln (38) it is not likely that the silicates of potassium or sodium were present to any marked extent as such, prior to evaporation. These investigators, by studying the freezing point and electrical conductivity of solutions of the simple alkali silicates, showed that the hydrolysis into the hydroxide and colloidal silicic acid is practically complete in concentrations up to 1 gram-molecule of the silicate per 48 liters of solution.

Reaction with carbonic acid. Silicate decomposition by carbonated water results in the formation, in the main, of the same final products as by reaction with pure water, except that the alkalies and alkaline earth metals appear as the carbonates or bicarbonates. Beginning with the early work of Rogers (54) the majority of investigations indicate a greater degree of solubility of the silicate minerals in water containing CO_2 than in pure water. With carbonated water, as with pure water, the amount of direct contact of mineral with reagent is of great importance, as is shown by Bassalik's (4, 5) work. Bassalik studied the solvent action upon various minerals of bacterial activity. Pure cultures of many organisms were grown in suspensions of the minerals, after which the filtrates were analyzed. *Bacillus extorquens*, a CO_2 producer, dissolved from 4 to 40 times as much orthoclase as any other CO_2 producer studied, although some of the others, including yeast, produced much larger amounts of CO_2. This is accounted for by the fact that *B. extorquens* grows directly upon the mineral particles, enclosing the mineral and colony in a zoogleal excresence, thus affording more intimate contact of the CO_2 and the mineral particles. Van Hise (66), in his comprehensive work upon metamorphism, ascribes by far the largest number of natural alterations of rocks to the action of CO_2 and water combined.

Reaction with salts. This reaction might be expected to effect some solution of the potassium of potassium-containing silicates, through the replacement of the mineral potassium by the basic ion of the soluble salt. Lemberg's (43, 43a) careful researches show that reactions of this character take place most rapidly and go much nearer to completion under fusion conditions. When aqueous solutions and suspensions are used, increasing the temperature accelerates the reactions greatly. Exchange of bases was brought about to a considerable degree in most cases within one month at 100°C., but at ordinary temperature the reactions were very incomplete. It may be noted that fusion of silicates with other compounds and also heating such mixtures to varying temperatures with superheated steam under pressure are the bases of many of the patented processes mentioned in another part of this paper. Lemberg also noted that the common bases have different replacing powers, potassium being strongest,

followed by magnesium, sodium and calcium in the order named. Thus it was found much easier to convert a sodium mineral into the corresponding-potassium mineral, than to bring about the reverse reaction. This replacing power holds for the soil mass as well as for the individual minerals, and the point is illustrated by drainage water analyses at Rothamsted (42) and elsewhere, where calcium is present in largest amounts and potassium in the smallest quantities.

All of these observations point to the great difficulty of liberating appreciable quantities of potassium from the primary minerals by means of the so-called exchange of bases, under soil conditions. The liberation in the soil of potassium for plant growth from the primary minerals must be left to the natural process of weathering (19, 31, 61) some of the most important forces of which are the solvent action of water, of CO_2 and of other products of biological activity. Of the last-named, the nitrous acid formed in nitrification is important (4, 5).

Secondary minerals and absorption. When the primary minerals are attacked by various solvent agents the amount of mineral decomposed is greater than would be indicated by the potassium which may be extracted by water (4, 5). This is accounted for as follows. A part of the potassium which is liberated as the hydroxide or carbonate is at once absorbed by the kaolinite formed in the initial reaction (16). This absorption is partly physical, a result of the colloidal nature of the siliceous products of decomposition, but secondary chemical reactions also occur. Similar "absorption-reactions" occur when stable salts of the alkali metals, as the sulfate or chloride, are added to colloidal material. In such cases the metal is usually absorbed as the hydroxide, leaving a pronounced acidity in the solution. While this is the general rule, exceptions occur, depending upon the nature of the colloid and of the salt used (27, 44, 65, 68).

The abundance of colloidal substances and of kaolinite in the average soils makes possible their very great absorptive capacity for potassium. Way (67) was the first to observe the absorption of bases by clay and the practical agricultural application of this phenomenon. Many methods have been devised for determining the so-called "immediately available," "remotely available or reserve" and "unavailable" potassium of soils. These consist for the most part of extraction with water or other solvents such as certain organic and mineral acids of varying concentrations and solutions of various salts. While these methods are purely arbitrary, and for that reason can scarcely be said even to give approximately the availability of soil potassium to the various crops, they do enable one to distinguish roughly the proportions of absorbed potassium, of the potassium of secondary minerals and of that contained in primary minerals in the soil. They are therefore not without value. The work of Fraps and his associates (22, 23) and of Frear and Erb (24) is of interest from this point of view.

The results of chemical researches and of plant culture experiments lead to the conclusions: (a) that the weaker solvents extract the potassium which is contained in the secondary soil minerals and that which may be temporarily held by physical absorption, but only a very small fraction of the potassium of the native minerals; and (b) that while crops may draw upon the unweathered, primary minerals for a portion of their potassium in emergencies, they rely in the main upon the absorbed potassium and secondary minerals for their supply (6, 7, 22, 23, 24, 37, 40, 49, 51, 53, 62, 63).

IV. EXPERIMENTAL

General plan of experiments

The four experiments here reported were carried out for the purpose of obtaining information on the following questions:

1. Will applications of primary potassium-containing minerals to peat soil affect the yield of crops grown therein?
2. To what extent are crops enabled to obtain potassium from those minerals?
3. Is the availability of the mineral potassium for plants affected by the presence of decomposing active organic material, or of magnesium or sodium chloride?
4. What are the effects of decomposing organic material and of magnesium and sodium chlorides upon the amount of potassium which can be extracted by water from these minerals under soil conditions?
5. What effect does decomposing organic matter have upon the solubility of the mineral potassium in the absence of soil?
6. What is the explanation of the low availability of the potassium of dune sand?

Description of materials used

The soil used was a very loose peaty soil obtained from an area several hundred acres in extent near Manito, Illinois. It was quite free from sand and from roots or other residues of recently grown plants. It had been under cultivation for several years but had not been cropped more than once or twice within the last six or seven years. The last fertilizer treatment it had received was an application of KCl 14 years before the collection of soil for these experiments. The reaction was practically neutral, the lime-requirement as determined by the Hopkins method being 285 pounds $CaCO_3$ per acre. It contained 0.411 per cent of total potassium, or 4110 pounds per acre (1 million pounds peat soil assumed as the weight of an acre—$6\frac{2}{3}$ inches).

The minerals selected for study were orthoclase feldspar from San Diego County, California, microcline from Pennsylvania, leucite rock from the Leucite Hills, Wyoming, alunite from Utah, muscovite from North Carolina and lepidolite from the Black Hills of South Dakota. The impossibility of grind-

ing a large enough amount of muscovite sufficiently fine with the apparatus available necessitated its omission from the experiments. The ignited alunite was prepared by igniting to a bright red heat in a muffle furnace for two hours, until SO_2 fumes were no longer given off. The minerals used contained the following amounts of total potassium (K).

	per cent		*per cent*
Orthoclase	11.00	Alunite	8.32
Microcline	11.23	Ignited alunite	13.72
Leucite	9.49	Lepidolite	8.99

The limestone used was high-calcium stone containing 0.21 per cent K and approximately 92 per cent $CACO_3$.

The organic materials used were: (a) bright clean alfalfa hay, finely ground (legume), (b) clean prairie hay, consisting mainly of blades, finely ground (non-legume) and (c) fresh cow manure, without litter, carefully dried at low temperature and ground. For experiments II and III the manure was used fresh, without drying.

The chemicals were high-grade analyzed chemicals from the laboratory stock.

Experiment I. Effect of potassium-containing minerals on yield and composition of buckwheat crop

Six series of plant cultures were grown in 4-gallon glazed earthenware jars provided with drainage outlets. Each jar was filled with peat soil equivalent to 3039 gm. water-free soil. All received limestone, finely ground, at the rate of 1 ton per acre, or 12.5 gm. per jar, based upon the area of the jar. Series 100 was a check series and received no minerals. Series 200 to 600 received orthoclase, microcline, leucite, alunite and lepidolite, respectively, at the rate of 25 gm. per jar, or 2 tons per acre. The only exception to this is that jars 1a and 2a in each series received 125 gm., or 10 tons per acre. Additional treatments were applied to the jars of each of the six series as indicated in the following table:

Table showing applications to crop culture jars in addition to minerals

NUMBER OF JAR	SUBSTANCE ADDED	POUNDS PER ACRE	GRAMS PER JAR
1, 2	Nothing		
1a, 2a	Mineral alone, 10 tons	20,000	125.0
1b, 2b	Mineral alone, ignited	2,000	25.0*
3, 4	Alfalfa	6,000	37.5
5, 6	Prarie hay	6,000	37.5
7, 8	Cow manure	3,536	22.1†
9, 10	$MgCl_2.6H_2O$	800	5.0
11, 12	NaCl	500	3.1
13, 14	KCl	200	1.25‡

* Series 500 (alunite) only.

† 22.1 gm. air-dry manure equivalent to 125 gm. fresh manure, or 20,000 pounds per acre.

‡ Series 100 (check) only.

All of the 43 treatments were carried out in duplicate. The jars were planted to buckwheat April 22, 1918, and as soon as the plants were two to three inches high they were thinned to 11 plants per jar. The moisture content was maintained at approximately 160 per cent of the water-free weight of soil. The plants grew vigorously throughout the season, except in series 600, in which they did not thrive as well as in series 100, the next poorest. Numbers 601a and 602a, which received the heavy application of lepidolite were especially stunted, the leaves being small, yellow and curled. Little difference could be observed in the growth of the plants in series 200, 300, 400 and 500.

The crops were harvested on July 25 and preserved in cheesecloth bags until air-dry. They were then weighed, the crops from duplicate jars combined, finely ground, and preserved in tightly stoppered jars for analysis. Table 1 gives the yields from all the jars, the per cent of potassium in the crops, and the amount of potassium removed from each jar.

In experiments II and III the amount of water-soluble potassium which could be extracted from the peat soil by shaking with an excess of water was determined at two different times on aliquots of the same sample, kept under optimum moisture conditions. The water-soluble potassium of the organic materials was determined by the same method. These amounts were:

	Part of total K which is soluble per cent
For peat soil, initial, 37.7 mgm. K per 100 gm. water-free soil	9.17
For peat soil 80 days later, 33.9 mgm. K per 100 gm. water-free soil	8.25
For alfalfa, 15.4 mgm. K per gram of dry matter	96.25
For prairie hay, 8.4 mgm. K per gram of dry matter	97.68
For cow manure, 6.6 mgm. K per gram of dry matter	100.00

There are three sources of soluble potassium for the crop, which can thus be measured, that in the soil, that in the organic materials added (or KCl in 113 and 114), and that in the seeds planted. The total potassium added per jar in the seeds planted was 2 mgm., all of which is reckoned as available. By difference the potassium obtained by the crop from insoluble sources can be calculated. These amounts are recorded in the last column of table 1 (+) as well as any excess of soluble potassium in the soil which the crop did not take up (−).

Discussion of results

The relative increases in yield produced by applications of the minerals are quite large, as shown by the percentage calculations recorded in table 2. Lepidolite gives unsatisfactory returns, but with the other four minerals only one case is found in which the yield is less than with the same treatment minus the mineral (jars 209, 210), and here the variation in duplicates is wider than that in the two treatments. That these increases in yield were produced by the mineral rather than by the auxiliary treatment is indicated by table 3.

TABLE 1

Yield and potassium content of buckwheat in experiment I

NUMBER OF JAR	YIELD OF CROP	AVERAGE YIELD	K IN CROP	K REMOVED FROM JAR	SOLUBLE K FROM ALL SOURCES	K OBTAINED FROM INSOLUBLE SOURCES
			Series 100. Check			
	gm.	*gm.*	*per cent*	*gm.*	*gm.*	*gm.*
101	52.9					
102	55.3	54.1	1.96	1.060	1.148	−0.088
103	66.5					
104	55.4	60.9	2.07	1.261	1.725	−0.464
105	46.7					
106	40.2	43.4	2.37	1.028	1.463	−0.435
107	44.5					
108	57.8	51.1	2.24	1.146	1.294	−0.148
109	48.8					
110	54.9	51.8	2.21	1.145	1.148	−0.003
111	37.2					
112	50.8	44.0	2.43	1.069	1.148	−0.079
113	59.3					
114	61.9	60.6	1.88	1.140	1.803	−0.663
			Series 200. Orthoclase			
201	68.3					
202	76.1	72.2	1.87	1.350	1.148	+0.202
201a	72.1					
202a	66.4	69.2	1.95	1.350	1.148	+0.202
203	65.5					
204	61.8	63.6	2.67	1.698	1.725	−0.027
205	59.7					
206	57.4	58.5	2.23	1.305	1.463	−0.158
207	69.5					
208	71.6	70.5	2.17	1.530	1.294	+0.236
209	42.3					
210	55.1	48.7	2.32	1.130	1.148	−0.018
211	52.6					
212	59.9	56.2	2.34	1.315	1.148	+0.167

TABLE 1—*Continued*

NUMBER OF JAR	YIELD OF CROP	AVERAGE YIELD	K IN CROP	K REMOVED FROM JAR	SOLUBLE K FROM ALL SOURCES	K OBTAINED FROM INSOLUBLE SOURCES
			Series 300. Microcline			
	gm.	*gm.*	*per cent*	*gm.*	*gm.*	*gm.*
301	76.0					
302	75.6	75.8	1.69	1.281	1.148	+0.133
301a	75.5					
302a	65.0	70.2	1.80	1.264	1.148	+0.116
303	75.2					
304	61.9	68.5	1.90	1.302	1.725	−0.423
305	61.7					
306	57.8	59.7	1.95	1.164	1.463	−0.299
307	77.2					
308	68.0	72.6	2.00	1.452	1.294	+0.158
309	60.5					
310	63.0	61.7	1.78	1.098	1.148	−0.050
311	50.6					
312	53.0*	51.8	1.59	0.855	1.148	−0.293
			Series 400. Leucite			
401	71.2					
402	80.3	75.7	1.63	1.234	1.148	+0.086
401a	79.4					
402a	76.4	77.9	1.75	1.363	1.148	+0.215
403	71.2					
404	69.2	70.2	2.32	1.629	1.725	−0.096
405	78.3					
406	56.1	67.2	1.72	1.155	1.463	−0.308
407	74.0					
408	71.8	72.9	1.66	1.210	1.294	−0.084
409	64.9					
410	66.2	65.5	1.86	1.218	1.148	+0.070
411	59.3					
412	61.6	60.4	2.15	1.298	1.148	+0.150

* Stand of only 2 plants.

TABLE 1—*Concluded*

NUMBER OF JAR	YIELD OF CROP	AVERAGE YIELD	K IN CROP	K REMOVED FROM JAR	SOLUBLE K FROM ALL SOURCES	K OBTAINED FROM INSOLUBLE SOURCES
			Series 500. Alunite			
	gm.	*gm.*	*per cent*	*gm.*	*gm.*	*gm.*
501	74.7					
502	77.9	76.3	1.73	1.320	1.148	+0.172
501a	72.3					
502a	72.4	72.3	1.72	1.244	1.148	+0.096
501b	63.8					(−2.999*)
502b	62.4	63.1	2.47	1.559	1.148	+0.411
503	72.4					
504	66.9	69.6	2.27	1.580	1.725	−0.145
505	62.0					
506	60.1	61.0	1.75	1.068	1.463	−0.395
507	68.7					
508	69.3	69.0	1.92	1.324	1.294	+0.030
509	63.6					
510	72.8	68.2	1.93	1.316	1.148	+0.168
511	67.2					
512	67.0	67.1	1.92	1.288	1.148	+0.140
			Series 600. Lepidolite			
601	58.7					
602	60.5	59.6	2.06	1.227	1.148	+0.079
601a	27.9					
602a	33.6	30.7	2.39	0.735	1.148	−0.413
603	60.0					
604	50.4	55.2	2.21	1.220	1.725	−0.505
605	52.6					
606	47.6	50.1	2.60	1.302	1.463	−0.161
607	65.2					
608	63.6	64.4	2.00	1.288	1.294	−0.006
609	45.8					
610	47.5	46.6	1.94	0.903	1.148	−0.245
611	51.9					
612	51.8	51.8	1.95	1.010	1.148	−0.138

* This value is obtained if the potassium of ignited alunite is considered entirely available.

In this table the relative yields in each series are calculated as percentages of the yield produced by the mineral alone, which is taken as 100. Almost without exception the yield is greater with the mineral alone than where any of the additional treatments were applied.

The value of the decaying organic manures in liberating potassium is unfairly minimized, however, if yields alone are taken as a criterion. The value

TABLE 2

Relative yields of buckwheat. Effect of minerals (no mineral = 100)

JAR NUMBER	AUXILIARY TREATMENT	SERIES 100, NO MINERAL	SERIES 200, ORTHOCLASE	SERIES 300, MICROCLINE	SERIES 400, LEUCITE	SERIES 500, ALUNITE	SERIES 600, LEPIDOLITE
1, 2	None	100	133.5	140.2	139.9	141.0	110.2
1a, 2a	10 tons mineral		127.9	129.7	144.0	133.7	56.7
1b, 2b	Ignition of mineral					116.6	
3, 4	Alfalfa	100	104.4	112.5	115.3	114.3	90.6
5, 6	Prairie hay	100	134.8	137.6	154.8	140.3	115.4
7, 8	Cow manure	100	138.0	142.1	142.7	135.0	126.0
9, 10	$MgCl_2.6H_2O$	100	94.0	119.1	126.5	131.7	90.0
11, 12	NaCl	100	127.7	122.3	137.3	152.5	117.7
13, 14	KCl	112					
Average.....		100	121.1	128.3	134.8	133.1	107.3

TABLE 3

Relative yields of buckwheat. Effect of auxiliary treatment (mineral alone = 100)

JAR NUMBER	AUXILIARY TREATMENT	SERIES 100, NO MINERAL	SERIES 200, ORTHOCLASE	SERIES 300, MICROCLINE	SERIES 400, LEUCITE	SERIES 500, ALUNITE	SERIES 600, LEPIDOLITE	AVERAGE
1, 2	None	100.0	100.0	100.0	100.0	100.0	100.0	100.0
1a, 2a	10 tons mineral		95.8	92.6	102.9	94.7	51.5	87.5
1b, 2b	Ignition of mineral					82.7		
3, 4	Alfalfa	112.6	88.1	90.4	92.7	91.2	92.6	94.9
5, 6	Prairie hay	80.2	81.0	78.7	88.8	79.9	84.1	82.1
7, 8	Cow manure	94.4	97.7	95.8	96.4	90.4	108.1	97.1
9, 10	$MgCl_26H_2O$	95.7	67.4	81.4	86.5	89.4	78.2	83.1
11, 12	NaCl	81.3	77.8	68.3	79.8	87.9	86.9	80.3
13, 14	KCl	112.0						

of decomposing organic matter in dissolving relatively insoluble mineral plant nutrients is generally ascribed largely to the HNO_2 produced in nitrification, organic acids produced by partial decomposition of non-nitrogenous compounds, and CO_2. The large excess of limestone applied to all the jars furnished an abundance of readily available base for the neutralization of these acids, thus preventing them from attacking the less soluble potassium silicates. This fact was realized at the beginning of the work, but it was believed that

the beneficial effect of the limestone in the soil to the growing crop would cause sufficiently increased root growth and feeding power of the plant to offset the disadvantage. The data of these experiments furnishes no basis for a comparison of these values. Furthermore, the large amount of organic matter of the peat itself was probably decomposed rapidly enough to affect the minerals to almost if not quite as great an extent as the small amount of organic material added. Indications of considerable nitrification were furnished by the appearance occasionally during the growing season, of a slight white or brownish crust of nitrates and other salts on the surface of the soil in all the jars.

An inventory of the sources of potassium, soluble and insoluble, upon which the crops could draw for their supply indicates that the deficiency of available potassium in this soil is not as great as is to be desired in an experiment of this kind. The soluble potassium in the soil alone, according to the extraction and analysis noted previously, amounts to 1.146 gm. per jar. The amount of soluble potassium added in the organic materials is, for the jars receiving those materials, 0.755 gm. in the alfalfa, 0.315 gm. in the prairie hay and 0.146 gm. in the manure. The 0.002 gm. of potassium added in the seed is considered available, and the sum of these three amounts gives the values recorded in the next to last column of table 1. This leaves insoluble potassium in the soil of each jar, 11.314 gm.; in the limestone added 0.026 gm. and in the minerals added, 2.08 to 2.81 gm. except where the 10-ton applications were made, in which there was five times as much. In calculating the values for the last column of table 1 it was assumed that the crop utilizes all the potassium from the soluble sources named before beginning on the insoluble supply. It may be noted that in 25 of the 43 cultures, a part of the soluble potassium amounting to from 3 to 663 mgm. remained in the jars, unused by the plant, while in only 18 jars the plants utilized a part of the insoluble potassium. These unused reserves of soluble potassium were present mainly in series 100 and 600, where the yields were small, and the crops more or less unthrifty in appearance. In the other four series the unused reserves were found, mainly, in the jars receiving an excess of soluble potassium in the organic manures added.

The percentage of potassium in the crops from the various treatments varies widely. These variations appear to depend as much upon the available supply of potassium as upon the crop yield. The total amount removed per jar, on the other hand, is necessarily dependent upon the yield to a large extent. As a result, the high yields are accompanied by the removal of some potassium from the sources listed as insoluble, except where an abundant supply of soluble potassium has been added in the organic materials. The maximum amount of "insoluble" potassium thus taken up by the plants, was in jars 401a and 402a, where the potassium from insoluble sources constituted 15.8 per cent of the total amount taken up by the crop.

The effect of the minerals upon the amount of potassium utilized by the crop may be shown very clearly by averaging the amounts of potassium removed per jar for each series separately. The following table gives these averages,

as well as the relative amounts removed per jar on a basis of 100 for the series receiving no mineral:

SERIES	K REMOVED PER JAR, AVERAGE OF 14 JARS	RELATIVE AMOUNT OF K REMOVED PER JAR, AVERAGE OF 14 JARS
	gm.	
100, No mineral	1.118	100.0
200, Orthoclase	1.383	123.7
300, Microcline	1.202	107.5
400, Leucite	1.301	116.3
500, Alunite	1.306*	116.8*
501b, 502b, Ignited alunite	1.559	139.5
600, Lepidolite	1.098	98.26

* Average of 16 jars.

Increased amounts of potassium are thus seen to be removed by the crops, amounting to 7.5 to 23.7 per cent where minerals are supplied, if we exclude ignited alunite, which contains much soluble potassium, and lepidolite, which shows unsatisfactory results here as in the yields. This method of averaging is not unfair, because the values averaged are from jars receiving the same supplementary treatments in each series.

These observations lead to the following conclusions:

1. Applications of 25 gm. per jar (approximately 2 tons per acre) of orthoclase, microcline, leucite and alunite increase the yield of buckwheat from 20 to 35 per cent and also enable the crop to utilize all the water-soluble potassium present as well as some of the less available forms. A part of this may come from the minerals applied.

2. On the peat soils used in this experiment the addition of crop residues, manure, or soluble magnesium or sodium salts does not increase the yield of buckwheat or the availablility of the potassium of the minerals added.

3. The activities of the root system through contact with the soil or mineral particles, and commonly spoken of as the "feeding power" of plants, is an important factor to be considered in the liberation of relatively insoluble potassium.

Experiment II. Solubility of the minerals in water as affected by decaying organic materials and soluble salts under soil conditions

This experiment was carried out in half-gallon Mason jars, loosely covered in order to prevent excessive evaporation and keep out dirt, without excluding air. It was the purpose to follow the general plan of Experiment I as to treatments, but to determine the potassium in a water extract instead of growing a crop in the soil. Since the absorbing power of a soil prevents as complete extraction of the water-soluble potassium as the plant is capable of, a larger proportion of mineral to soil was used than in the culture experiment. The

method of shaking the soil with a large excess of water was chosen in preference to the percolation method of extraction in order to lessen potassium absorption as much as possible.

To each 100 gm. of water-free soil was added enough mineral to carry 1 gm. of potassium. The organic materials were added at the rate of 1 gm. of dry matter per 100 gm. of soil and the soluble salts were added in molecular equivalents of the potassium contained in the mineral. In addition to the auxiliary treatments used in experiment I, NH_4Cl and dextrose were used. Table 4 gives the treatments in detail.

In each case double the amount of soil needed for an extraction was taken. The minerals and other substances were added to the air-dry soil (except soluble salts and dextrose) and well mixed, dry. Enough distilled water was

TABLE 4

Soil and treatments used in experiment II

JAR NUMBER	PEAT SOIL EQUIVALENT TO WATER-FREE SOIL	AUXILIARY TREATMENT		SERIES A, NO MINERAL	SERIES B, ORTHOCLASE	SERIES C, MICROCLINE	SERIES D, LEUCITE	SERIES E, ALUNITE	SERIES F, LEPIDOLITE
		Substance added	Amount						
	gm.		*gm.*		*gm.*	*gm.*	*gm.*	*gm.*	*gm.*
1	200	Nothing			18.32	17.81	21.07	24.04	22.24
2	200	$CaCO_3$	2.56		18.32	17.81	21.07	24.04	22.24
3	400	Alfalfa	4.26*		36.64	35.62	42.14	48.08	44.48
4	400	Prairie hay	4.29*		36.64	35.62	42.14	48.08	44.48
5	400	Fresh manure	23.91*		36.64	35.62	42.14	48.08	44.48
6	200	$MgCl_2.6H_2O$	5.20		18.32	17.81	21.07	24.04	22.24
7	200	NaCl	2.99		18.32	17.81	21.07	24.04	22.24
8	200	NH_4Cl	2.74		18.32	17.81	21.07	24.04	22.24
9	200	Dextrose	2.00		18.32	17.81	21.07	24.04	22.24
10	200	KCl	3.81						

* Equivalent to 4.00 gm. dry matter.

added to bring up to optimum (160 per cent) and again very thoroughly mixed. The soluble salts and dextrose were dissolved in the water used for making the soil up to optimum. The entire mass was then weighed, one-half removed for extraction and the other half placed in the Mason jars. The fractions kept in the jars were weighed and brought up to optimum moisture content every few days with distilled water during the period of the experiment. The double amounts of soil prepared in jars 3, 4 and 5 of each series were prepared in order that ammonia and nitrate nitrogen might be determined in the soils receiving organic manures. This might throw some light upon a possible correlation of ammonification, nitrification and solution of the potassium of the minerals used. Unfortunately, the determinations were all ruined by the breaking of a refrigerating machine and consequent flooding of the building with NH_3 fumes. A few nitrate determinations were saved but the results were not considered of sufficient importance to record.

The method of determining water-soluble potassium was as follows. The moist treated soils were immediately placed in 2½-liter bottles, shaken 5 hours in a mechanical shaker with 1500 cc. distilled water (including the water already contained in the sample) and then allowed to settle 36 hours. The supernatant solution was then filtered through filter paper and placed in glass stoppered bottles with a few drops of chloroform until used. Aliquots of this solution were clarified by shaking with 5 cc. of milk of lime. Aliquots of the

TABLE 5

Milligrams of potassium extracted by water from 100 grams of soil

JAR NUMBER	TREATMENT	A, CHECK NO MINERAL	B, ORTHOCLASE	C, MICROCLINE	D, LEUCITE	E, ALUNITE	F, LEPIDOLITE
		mgm.	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*
1	Nothing	37.7	26.6	26.6	32.0	28.5	39.8
		33.9	33.5	32.3	37.3	33.7	52.6
2	$CaCO_3$	32.9	33.7	32.0	35.3	32.4	46.2
		29.1	33.1	30.1	36.9	33.5	46.1
3	Alfalfa	39.1	40.3	34.6	39.6	35.7	51.9
		41.0	42.6	40.3	45.3	40.6	62.3
4	Prairie hay	31.7	32.8	28.8	30.7	31.4	50.8
		34.4	36.1	33.5	39.6	36.0	49.5
5	Manure	27.7	31.4	27.6	31.2	27.8	48.8
		33.0	36.4	35.0	39.8	35.3	53.1
8	NH_4Cl	29.8	43.7	41.3	45.9	42.4	62.9
		43.9	44.0	45.2	56.3	46.0	84.4
9	Dextrose	23.6	26.6	26.3	21.2	29.7	49.6
		29.7	31.2	28.1	37.4	31.1	48.4
10	KCl	184.6					
		176.4					

clarified solution were then filtered and taken to dryness in an excess of H_2SO_4, ignited to destroy organic matter, taken up in boiling water and thoroughly triturated with an agate pestle. Calcium sulfate was filtered off and washed, the remainder of the calcium was removed as the oxalate, ammonium salts driven off and potassium determined gravimetrically as K_2PtCl_6.

At the end of 80 days the second set of moist soil samples was removed from the jars, extracted and the extract analyzed for potassium in the same way. It was impossible in the limited time available to overcome difficulties caused by the interference of the large amounts of magnesium and sodium in numbers 6 and 7. The results are considered untrustworthy and are therefore not presented.

The results of the analyses are recorded in table 5, the figures representing milligrams of K per 100 gm. of water-free soil, or parts per 100,000. The upper row of figures represents the results from the initial water-extraction, and the lower row, results of extraction after 80 days of moist contact of soil and mineral under aerobic conditions.

Subtracting the values given in the check column, A, from those in each of the succeeding columns gives the increase in soluble potassium due to the addition of the minerals. These values are in table 6.

TABLE 6

Gains (+) in soluble potassium over check

JAR NUMBER	TREATMENT	MGM. K PER 100 GM. SOIL				
		B, Orthoclase	C, Microcline	D, Leucite	E, Alunite	F, Lepidolite
1	0	−11.1	−11.1	− 5.7	− 9.2	+ 2.1
		+ 0.4	− 1.6	+ 3.4	− 0.2	+18.7
2	$CaCO_3$	+ 0.8	− 0.9	+ 2.4	+ 0.5	+13.3
		+ 4.0	+ 1.0	+ 7.0	+ 4.4	+17.0
3	Alfalfa	+ 1.2	− 4.5	+ 0.5	− 3.4	+12.8
		+ 1.6	− 0.7	+ 4.3	− 0.4	+21.3
4	Prairie hay	+ 1.1	− 2.9	− 1.0	− 0.3	+19.1
		+ 1.7	− 0.9	+ 5.2	+ 1.6	+15.1
5	Manure	+ 3.7	− 0.1	+ 3.5	+ 0.1	+21.1
		+ 3.4	+ 2.0	+ 6.8	+ 2.3	+20.1
8	NH_4Cl	+ 3.9	+11.5	+16.1	+12.6	+33.1
		+ 0.1	+ 1.3	+12.4	+ 2.1	+40.5
9	Dextrose	+ 3.0	+ 2.7	− 2.4	+ 6.1	+26.0
		+ 1.5	− 1.6	+ 7.7	+ 1.4	+18.7

Discussion of results

The most striking fact brought out by table 5 is the large amount of soluble potassium in the untreated peat soil. From 8 to 9 per cent of the total potassium in the soil is extracted by shaking with water. This suggests that a considerable proportion of the soil potassium of the peat is held by the organic matter of the soil, since potassium which is bound to the mineral soil constituents is, as a rule, much more firmly held.

An apparent increase in the amount of soluble potassium after 80 days' standing is noted throughout table 5, almost without exception.

The effects of the minerals are most clearly shown in table 6. Three points are conspicuous.

(a) The solubility of lepidolite is very high throughout all the treatments. The solubility of lepidolite is influenced little or not at all by any of the treatments. In view of this result, the stunting of the crop grown in series 600 of experiment I may well be ascribed to the presence of some toxic element dissolved out of the mineral, probably an excess of soluble lithium. The excess of calcium carbonate in the soil, which was already practically neutral makes poisoning by soluble aluminum salts appear improbable.

(b) The addition of the minerals to the untreated soil (no. 1, table 6) caused an immediate disappearance of considerable amounts of potassium from solution which reappeared in the later extraction. This suggests a possible temporary absorbing capacity of the minerals themselves for potassium.

(c) The only evidence of potassium liberation by exchange of bases is furnished by the extraction with NH_4Cl. With the exception of orthoclase there is an increased amount of potassium dissolved to the extent of 11 to 33 mgm. per 100 gm. of soil over that with NH_4Cl alone (no mineral). The increase over the mineral alone is equally marked, as shown in table 5. This is in accord with the findings of André (2), Steiger (59) and Beyer (6). The solubility in all the other treatments is but slight, the values recorded being, for the most part, within the limits of experimental error. Leucite, however, shows distinctly greater solubility than orthoclase, microcline or alunite.

Concerning the auxiliary treatments, nothing can be said in their favor, used under the conditions of this experiment, except for the NH_4Cl already noted. Where the organic manures have been added, there is an increase in potassium extracted, but it should be noted that the increase is not sufficient to cover the amount added in the organic material. In every case the soil-mineral mixture has absorbed half or more of the soluble potassium added in the organic manures. Dextrose has depressed the solution of potassium throughout. $CaCO_3$ has had no effect except to decrease slightly the temporary absorption of potassium by the soil-mineral mixture. The absorptive power of the soil is shown in no. 10, table 5. The amounts of soluble potassium found indicate the immediate absorption by the soil of 81.5 per cent of the potassium added as KCl, this being increased to 82.4 per cent during the 80 days.

Experiment III. Solubility of minerals in water as affected by certain decaying organic materials

The general plan of experiment III is the same as in experiment II.

In experiment III mixtures of the minerals and the organic materials used in experiment II were allowed to stand moistened, but not saturated with water for 80 days. The method of mixing and of extracting was exactly the same as in experiment II. Each mineral was treated with two different proportions of the organic material. One was the same as in experiment II, namely, 1 gm. dry organic material to 1 gm. total K in mineral, while the other mixture contained 10 times as much organic matter. For the purpose of com-

parison, each of the organic materials and minerals was extracted with water separately. The results of these extractions are given in tables 7, 8, and 9. In table 7 the upper row of figures (a) represents the values obtained at the

TABLE 7

Water-soluble potassium in organic matter-mineral mixture

NUMBER	ORGANIC MATERIALS TAKEN	DRY MATTER	MGM. K PER 1 GM. TOTAL K IN MINERAL a = initial b = 80 days later (Mineral used = 10 gm. Total K)					
				B, Orthoclase	C, Microcline	D, Leucite	E, Alunite	F, Lepidolite
		gm.						
10	Alfalfa	10	a	17.8	16.5	19.2	16.5	36.0
			b	17.0	16.4	19.0	17.7	19.9
11	Alfalfa	100	a	139.1	132.1	134.0	129.2	150.0
			b	159.6	165.8	159.9	154.7	170.7
12	Prairie hay	10	a	11.0	9.5	12.7	9.3	22.5
			b	9.7	8.6	11.8	9.8	12.9
13	Prairie hay	100	a	72.5	82.1	82.8	85.2	103.7
			b	81.5	80.8	85.4	80.5	77.0
14	Manure	10*	a	8.0	7.6	10.4	6.9	19.3
			b	7.7	8.0	11.0	7.1	13.7
15	Manure	100*	a	49.4	30.7	42.3	63.4	78.3
			b	57.2	58.4	69.0	68.6	69.7

* Equivalent amount of fresh manure was used.

TABLE 8

Water-soluble potassium in organic materials used

SUBSTANCE	TOTAL K	WATER-SOLUBLE K	PER CENT OF TOTAL K WHICH IS SOLUBLE
	*per cent**	*per cent**	
Alfalfa	1.60	1.54	96.25
Prairie hay	0.86	0.84	97.68
Fresh manure	0.66	0.66	100.00

* Percentage in dry matter.

initial extraction, and the lower row (b) the values obtained 80 days later. In order to show the gain or loss of soluble potassium occasioned by contact of the minerals and organic matter, the sum of the values given in tables 8 and 9 was deducted from those in table 7. Table 10 gives the differences.

Discussion of results

An examination of the data in table 10 reveals the following facts. Only where the larger amounts of organic materials are used is there a significant change in the amount of soluble potassium obtained. This is a disappearance of potassium from solution in all the initial extractions and in the later extrac-

TABLE 9

Water-soluble K *in minerals*

SUBSTANCE	MGM. SOLUBLE K PER 100 GM. MINERAL	MGM. SOLUBLE K PER 1 GM. TOTAL K
Orthoclase	11.99	1.1
Microcline	11.79	1.0
Leucite	42.73	4.5
Alunite	11.18	1.3
Lepidolite	62.99	7.0

TABLE 10

Gain or loss of soluble K *occasioned by mixing of organic materials with minerals*

a = initial b = 80 days later

NUMBER		B, ORTHOCLASE	C, MICROCLINE	D, LEUCITE	E, ALUNITE	F, LEPIDOLITE
		mgm.	*mgm.*	*mgm.*	*mgm.*	*mgm.*
10	a	+ 1.3	+ 0.1	− 0.7	− 0.2	−13.6*
	b	+ 0.5	0	− 0.9	+ 1.0	− 2.5*
11	a	−16.0*	−13.0*	−24.5*	−26.1*	−11.0*
	b	+ 4.5*	+10.8*	+ 1.4	− 0.6	+ 9.7*
12	a	+ 1.5	+ 0.1	− 0.2	− 0.4	+ 7.1*
	b	+ 0.2	− 0.8	− 1.1	+ 0.1	− 2.5*
13	a	−12.6*	− 2.9*	− 7.7*	− 0.1	+12.7*
	b	− 3.6*	− 4.2*	− 3.1*	− 4.8*	−14.0*
14	a	+ 0.3	0	− 0.7	− 1.0	+ 5.7*
	b	0	+ 0.4	− 0.1	− 0.8	+ 0.1
15	a	−17.7*	−36.3*	−28.2*	− 3.9*	+ 5.3*
	b	− 9.9*	− 8.6*	− 1.5	+ 1.3	− 3.3*

* The values so marked are the only ones in which the differences are greater than can be accounted for by experimental error.

tions of prairie hay and manure, in amounts up to 55 per cent (C15, initial) of that added in the organic material. Alfalfa during 80 days effected the solution of 4.5 mgm. K per gm. of total K in orthoclase, 10.8 mgm. in microcline and 9.7 mgm. in lepidolite. The greater solvent action of the alfalfa is due in part to the fact that it was decomposed much more rapidly than the other two

organic materials. Four weeks after the beginning of the experiment the alfalfa had broken down to such an extent that none of the plant structure was distinguishable, and the mass resembled the cow manure in appearance. A large proportion of the prairie hay, on the other hand, was but little changed in appearance even at the end of the 80 days. The high proportion of easily decomposable nitrogenous material in the alfalfa may also have been a factor affecting its solvent action. There is a possibility that this factor was really the presence of ammonia, since conditions were more favorable for ammonification than for nitrification.

The high solubility of lepidolite noted in experiment II is further illustrated here, but the potassium dissolved disappears from solution later, as shown by the second extractions. The slow absorption of dissolved potassium suggests

TABLE 11

Absorption of potassium by minerals. Milligrams of K *per gram of total* K *in mineral*

NUMBER	MINERAL	AMOUNT OF MINERAL USED (=1 gm. K)	SOLUBLE K ADDED AS KCl	SOLUBLE K IN MINERAL (TABLE 9)	TOTAL SOLUBLE K	SOLUBLE K FOUND	GAIN (+) OR LOSS (−) OF SOLUBLE K
		gm.	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*
1	Orthoclase	9.16	150	1.1	151.1	144.6	− 6.5
2	Orthoclase	9.16	300	1.1	301.1	290.2	−10.9
3	Orthoclase	9.16	5	1.1	6.1	6.4	+ 0.3
4	Microcline	8.906	150	1.0	151.0	139.7	−11.3
5	Leucite	10.54	150	4.5	154.5	140.3	−14.2
6	Alunite	12.02	150	1.3	151.3	143.6	− 7.7
7	Lepidolite	11.12	150	7.0	157.0	137.1	−19.9
8	Lepidolite	11.12	225	7.0	232.0	210.1	−21.9

chemical reaction with the mineral, possibly a replacement of lithium by potassium.

The disappearance of potassium from solution in this experiment can be accounted for in only two ways. Either the potassium of the organic matter, upon decomposition of the latter, is in part converted into insoluble forms, or it is absorbed by the mineral. In the case of the initial extractions, the disappearance of soluble potassium can be accounted for only by absorption by the minerals (see table 8).

To verify this point the following experiment was carried out. Portions of each of the minerals equivalent to 1 gm. of potassium were weighed out, definite amounts of soluble potassium added as KCl from an accurately made standard solution and made up to a volume such that the proportion of mineral to water was the same as in the extractions of experiment III. These were shaken 5 hours and allowed to stand 36 hours. Suitable aliquots of these extractions were then analyzed.

The results of this experiment are presented in table 11.

The results of this experiment furnish ample verification of the statements made above. The minerals have absorbed potassium in every case, except where the very small amount of potassium was added in no. 3. The amounts may fairly be compared with those in the upper row, a, of no. 11, table 10. Absorption by the mineral thus accounts for a large part of the potassium which disappeared from solution—more than half except for orthoclase and alunite.

Experiment IV. Availability of Potassium in Sandy Soils

In another part of this paper certain sandy soils of Illinois containing a large amount of potassium were mentioned as being similar to peat soils in one respect, i.e., in that they are deficient in available potassium. Experiment IV was undertaken in order to determine the reason for the low availability of the potassium in such soils. The cultural treatments consist of (a) whole sand as the cultural medium, (b) coarse separates (sands) and (c) a mixture of the

TABLE 12

Total and water-soluble K *in the different separates of sandy soil*

SUBSTANCE ANALYZED	TOTAL K	WATER-SOLUBLE K PER 100 GM. SOIL
	*per cent**	*mgm.*
Whole sand, unground	1.03	3.5
Coarse separates, 100-mesh	1.01	5.9
Fine separates	1.59	39.8

* Samples ground to impalpable powder for total potassium determination.

coarse separates and the same finely ground. Each jar receives a complete nutrient solution minus potassium.[1]

The whole sand and coarse and fine separates were examined in the laboratory as follows. A mechanical analysis showed that the sandy soil used contained 96.7 per cent of coarse separates (sands) and 3.3 per cent of fine separates (silt plus clay). Separations were made by sedimentation in distilled water. Determinations were made in the three materials of total potassium and also of water-soluble potassium. The latter was determined as in the preceding experiments by shaking together 100 gm. of soil and 1500 cc. of distilled water, potassium being determined in an aliquot of the extract. The results are given in table 12.

In view of the fact that the coarse separates were obtained by sedimentation in water, no water-soluble determination was made on this fraction, unground. The large volume of water necessary to wash out all the silt and clay from the sand (approximately 100 liters for the 100 gm. of silt and clay used in the extraction above) would wash out all soluble potassium, which would remain in the silt and clay on evaporation.

[1] The crop is not yet harvested.

The high absorbing power of the fine separates is here illustrated. The 3.5 mgm. of potassium soluble in the whole sand, when concentrated in the fine separates is not extracted, the fine separates from 100 gm. of sand yielding to extraction only 1.31 mgm. of potassium. Grinding the coarse separates liberates some potassium, but not enough to be of any practical value. The grinding of 1 ton of coarse separates to 100-mesh size and down would produce, according to the figures in table 12, 0.114 pound of soluble potassium.

The relatively small surface of the coarse particles of sandy soils of the type used in this experiment readily accounts for the low availability of the potassium in these soils (29).

V. SUMMARY

1. The use of finely-ground potassium-bearing minerals increases the yield of buckwheat in peat soil 21 to 34.8 per cent.

2. Lepidolite is detrimental to the growth of buckwheat, especially if present in large amounts.

3. The addition of crop residues, manure, or soluble sodium or magnesium salts to peat soil, together with the minerals used in this experiment, does not increase the yield of crop or the availability of the mineral potassium.

4. The so-called "feeding power" of the plant itself, through the activities of the root system, is an important factor in the utilization of relatively insoluble potassium.

5. The solubility of the minerals used, as determined by extraction with water, is very low, except that of lepidolite. The solubility is increased by ammonium chloride and also by the decomposition of alfalfa. The result in the latter case may be due to ammonification of the nitrogenous compounds in the alfalfa.

6. All the minerals used have the ability to absorb considerable amounts of potassium from solution. The absorption is probably physical to a large extent.

7. The low availability of the potassium of dune sand is due to the fact that most of the potassium is contained in the larger particles. The relatively small surface of the particles is sufficient explanation of the low solubility of the potassium contained in them.

8. The increase in solubility of the potassium in such sands produced by grinding is not sufficient to be of practical value.

9. The results of the crop culture work should not be taken as conclusive. They should be verified by repetition for several seasons with various other farm crops.

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RELATION OF THE MOISTURE EQUIVALENT OF SOILS TO THE MOISTURE PROPERTIES UNDER FIELD CONDITIONS OF IRRIGATION

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In studies of the water requirement of soils under irrigation, both for land being irrigated and for land for which the construction of irrigation systems is contemplated, some criterion which will furnish an index of the soil moisture properties is needed. Mechanical analyses of the soil are expensive to make and the results, given in the seven grades of soil particles, do not lend themselves to ready comparison except by general soil classes. A criterion is needed which can be expressed as a single factor and which can be determined fairly readily at small expense. The moisture equivalent as suggested by Briggs and McLane is intended to be such an index of the soil moisture properties.

Comparisons of the moisture equivalent with other soil properties have been made, usually under laboratory conditions. The following discussion is a comparison of the moisture equivalent with the critical moisture points of soils under the actual field conditions of irrigation practice, and is based on data secured by the author in the course of various field investigations of the water requirements of different soils and their irrigation practice. This work was done partly while the writer was in the employ of the Irrigation Investigations of the United States Department of Agriculture, but more largely in connection with his general engineering practice. In all cases, the determinations of the moisture equivalents have been made by the Division of Soil Technology of the University of California under the direction of Prof. C. F. Shaw.

The general field method has been to take soil moisture samples before and after irrigation in order to determine the amount of water retained by the soils. Notes on the soil and crop conditions were secured and special samples at wilting taken when feasible. The main purpose of the field work was the study of the water requirements of the soils under irrigation practice. The comparison discussed here was incidental to this main purpose, so that in many cases samples representing only a part of the moisture properties of a particular soil were secured.

The data given were secured from a wide range of soils under varying conditions of practice. In 1913 and 1914, about 7000 individual moisture deter-

minations from 44 fields with 9 moisture equivalents of typical soils were secured, near Billings, Montana. In 1915 about 700 individual soil moisture samples and 14 moisture-equivalent determinations were secured during a study of sandy soils on the Minidoka project in Idaho. The field work in these two investigations was done by the author for the United States Department of Agriculture. In 1917 about 1000 moisture and 54 moisture-equivalent determinations were secured in a study of a wide variety of soils on the Sunnyside project in Washington. In 1917 also about 450 soil-moisture and 50 moisture-equivalent samples were secured from irrigated lands near Reno, Nevada. In addition less extensive results were secured in 1918 on soils near Los Molinos, California and the results obtained by Israelsen (1) for soils in the Sacramento Valley, California, were used. The results discussed cover a total of 136 determinations of moisture equivalents varying in numerical value from 4.1 to 37.6.

Comparisons of four moisture conditions are made both for the surface foot of soil and for the average of the upper 5 feet of soil. These are the maximum field capacity, the normal field capacity, the usual moisture before irrigation and the wilting of the crop. The maximum field capacity applies to soils shortly after irrigation before the moisture distribution is complete or to soils where downward percolation is retarded by heavier soil strata. It does not cover soil saturation but represents a higher moisture content than would be secured under normal conditions. The normal field capacity would apply to soils of uniform character at from 1 to 3 days after irrigation when moisture distribution had become fairly complete, although both evaporation from the soil and deep percolation may be continuing but at a lessened rate. The usual moisture before irrigation represents the minimum moisture under good practice where irrigation would be given just ahead of the actual needs of the crops. The wilting of the crop represents actual injury, practically the minimum to which moisture may be reduced.

In assembling the observations the soil moisture results were expressed in terms of the percentage of the moisture equivalent. The moisture equivalents were grouped by variations of 2.5 per cent. In the figures given the individual results are plotted and also the mean result for each group, the numbers with the means indicating the number of observations included in the mean. As all four soil-moisture points were not determined for the larger proportion of the individual soils, the number of points in the means is less than the total number of moisture-equivalent determinations in each group. This is particularly true for the means for the 5-foot depths of soil, as many soils included in the field work were of shallow depth or variable subsoil which prevented securing means for the full 5 feet.

In figure 1 the relation of soil moisture in the surface foot under field conditions to the moisture equivalent is given for the four moisture points. In order to indicate the variation of the individual results broken lines are drawn which represent 10 per cent variation from the mean curves. The greater

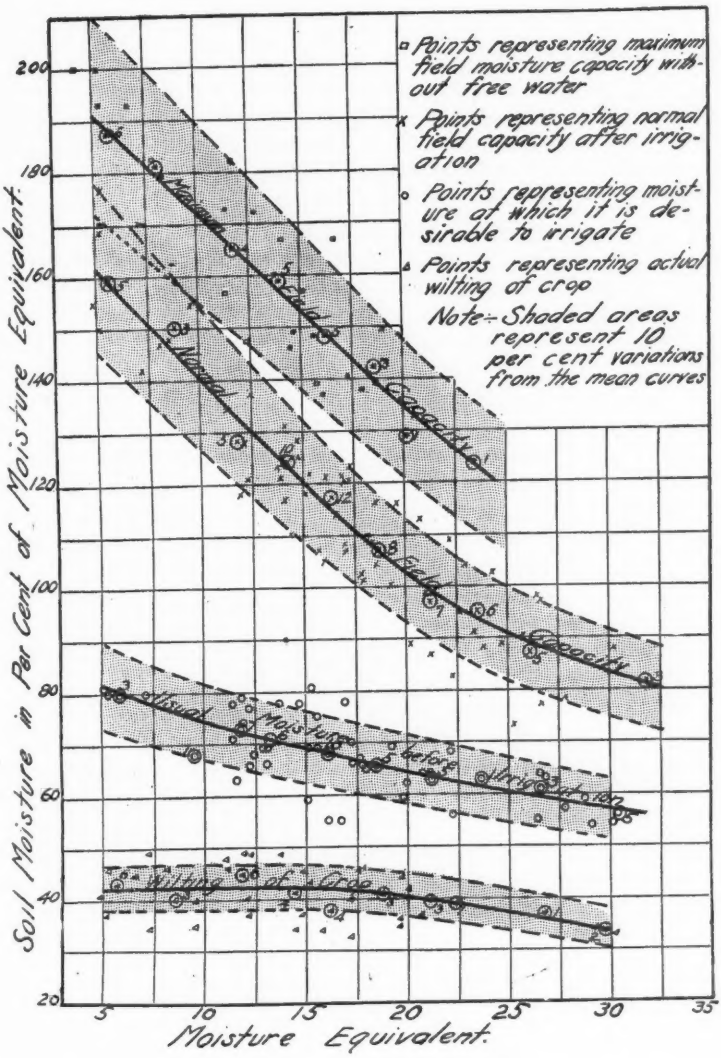

FIG. 1. RELATION OF SOIL MOISTURE IN SURFACE FOOT UNDER FIELD CONDITIONS TO THE MOISTURE EQUIVALENT

proportion of the observations fall within 10 per cent of the mean. The general relationships appears to be fairly consistent.

The variations of individual results may be due either to a lack of consistency of the moisture equivalent as an index of moisture properties or to a lack of accuracy in the selection of soil moisture samples representing the critical moisture points given. In the author's opinion, the latter source of error is the more probable one. The moisture condition at which a soil needs irrigation is not an exact one, particularly when the surface foot only is considered. It will vary for a given soil with the character of crop and its state of growth and with the moisture and soil conditions in the subsoil. Wilting is also a progressive process and the point at which the crop will fail to revive is difficult of actual determination. After irrigation, soil evaporation will continue at diminishing rates over several days, deep percolation may also continue for a considerable period. During this time the crop is withdrawing moisture for its use so that there is no definite point at which soil moisture samples can be expected to give the exact amount of moisture available for crop use.

It is thought that the results as plotted in figure 1 indicate as consistent a relationship between the moisture equivalent and the soil moisture under field conditions as is to be expected under the circumstances under which the observations were made. The purpose of the comparison was to determine whether such a general relationship exists rather than to express the relationship in definite numerical terms, and any specific numerical deductions from these curves, such as those given later in this discussion, should be considered as suggestive only and as subject to modification as additional numerical data may become available.

In figure 2 curves similar to those in figure 1 are given, except that the comparison is based on the mean moisture in the upper 5 feet of soil. The number of points available was less than of those used in figure 1 and the resulting mean curves are in consequence less definite in both their general form and their actual location than those for figure 1.

The curves given indicate that the relationship between field moisture properties and the moisture equivalent is not a linear one except possibly for conditions approaching wilting. Briggs and McLane have derived the formula

$$\textit{Wilting coefficient} = \textit{moisture equivalent} \div 1.84.$$

This formula was based on experiments where the plants were grown in limited volumes of soil rather than under normal field conditions. The above formula is equivalent to the wilting coefficient equalling 54.4 per cent of the moisture equivalent. The results given on figures 1 and 2 indicate that, at least under field conditions, the crops can reduce the soil moisture of both the surface foot and of the mean for the upper 5 feet below this amount. The mean of all observations on wilting for the surface foot of soil is about 40 per cent of the moisture equivalent.

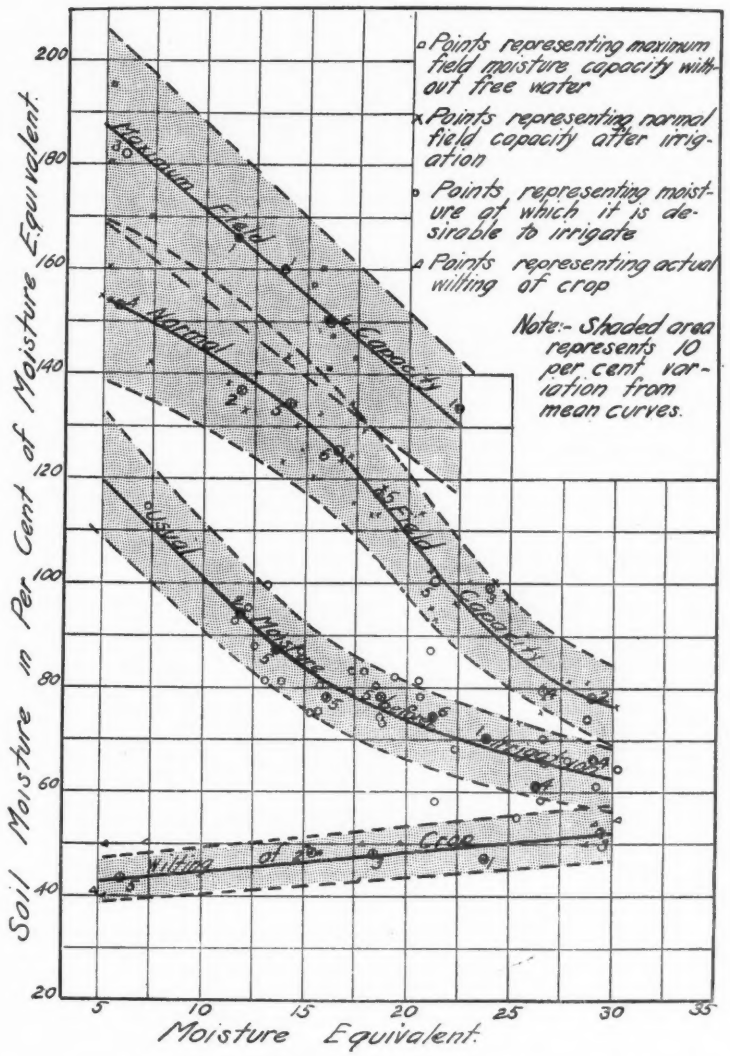

FIG. 2. RELATION OF SOIL MOISTURE IN UPPER 5 FEET OF SOIL UNDER FIELD CONDITIONS TO THE MOISTURE EQUIVALENT

Similarly Briggs and McLane have given the equation

Moisture-holding capacity = moisture equivalent × *1.57* + *21.*

The moisture-holding capacity used in this formula is based on the Hilgard short-tube method and exceeds the moisture capacity under field conditions of soils free to drain. In no case does the maximum field capacity reach the amount indicated by this formula.

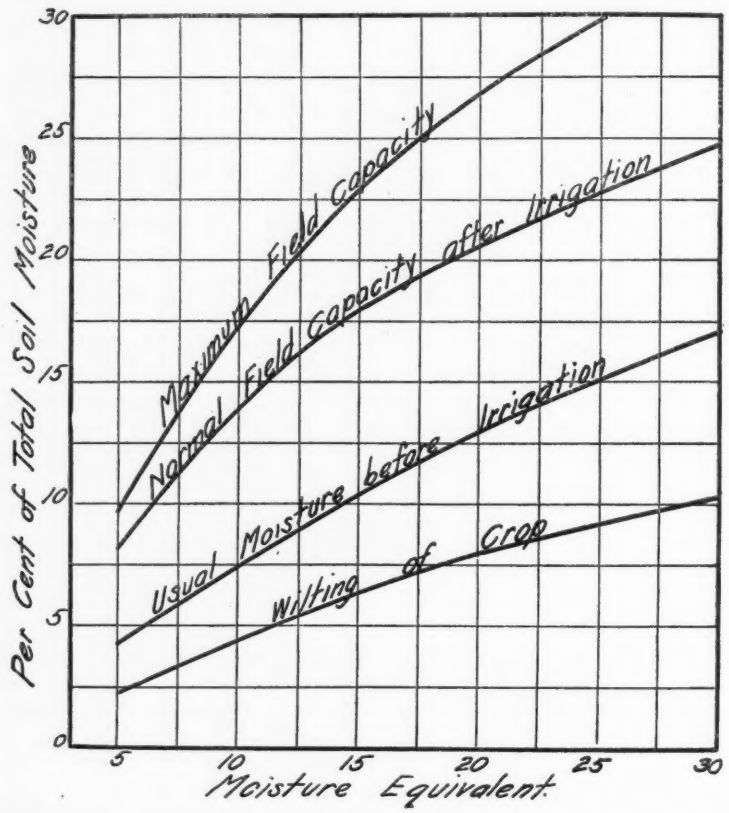

FIG. 3. RELATION OF PER CENT OF TOTAL MOISTURE IN SURFACE FOOT OF SOIL UNDER FIELD CONDITIONS AND MOISTURE EQUIVALENTS

In figures 3 and 4 the mean curves of figures 1 and 2 are redrawn, the percent of soil moisture being used directly instead of as a percentage of the moisture equivalent. These curves indicate the percentages of soil moisture on the oven-dry basis at the different critical-moisture points.

In figures 5 and 6 the curves of figures 3 and 4 are used to give the water added by usual irrigations. In figure 5 is plotted the difference in moisture before and after irrigation as shown for usual practice on figures 3 and 4. This shows the largest moisture capacity for 5 feet of soil in soils of medium texture. The coarse soils having a low moisture equivalent have a relatively small moisture-holding capacity. The heavy soils while having a

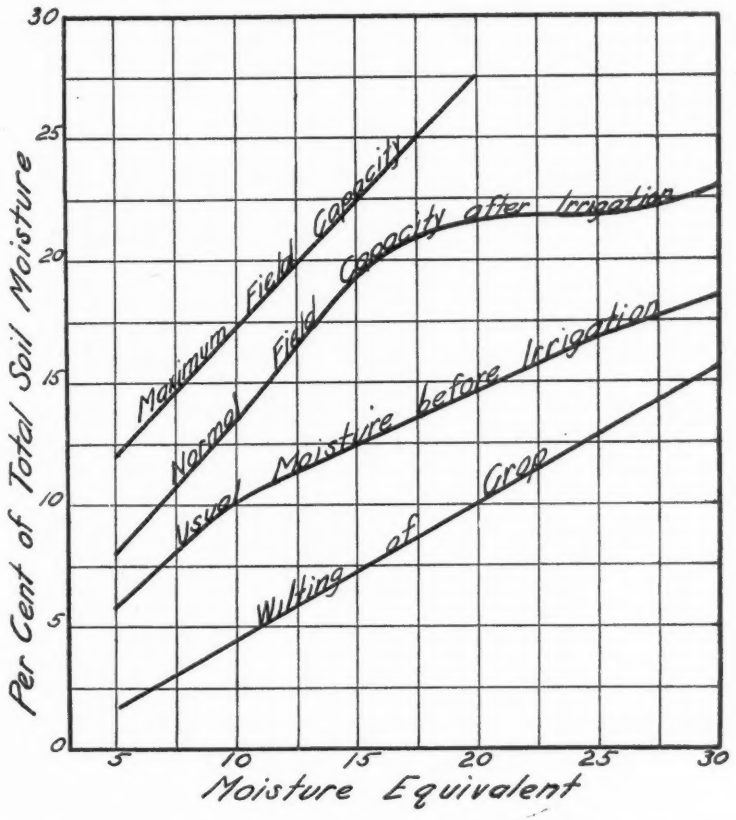

FIG. 4. RELATION OF PER CENT OF TOTAL MOISTURE IN UPPER 5 FEET OF SOIL UNDER FIELD CONDITIONS AND MOISTURE EQUIVALENTS

relatively large moisture-holding capacity, are not able to utilize this capacity to the 5-foot depth, because of the difficulty in getting full penetration. This difficulty in getting full penetration does not affect the surface foot, and the per cent of moisture added from an irrigation continues to increase with an increase in the moisture equivalent.

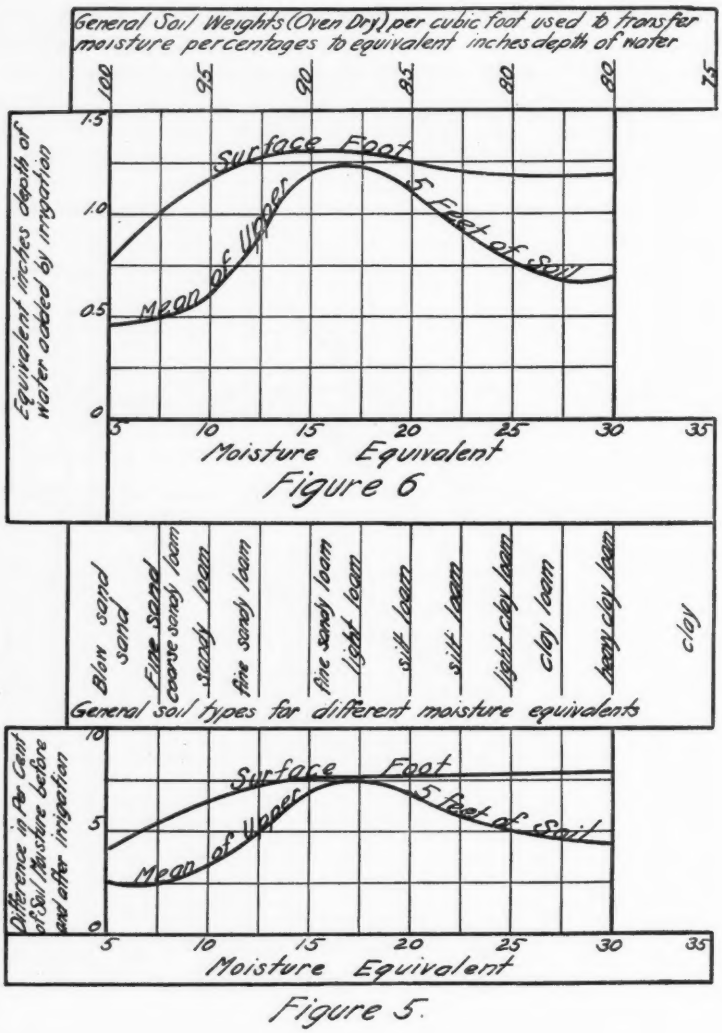

FIG. 5. RELATION OF PER CENT OF MOISTURE ADDED BY IRRIGATION UNDER FIELD CONDITIONS AND THE MOISTURE EQUIVALENTS

FIG. 6. RELATION OF EQUIVALENT INCHES DEPTH OF WATER RETAINED PER FOOT DEPTH OF SOIL FROM AN IRRIGATION AND THE MOISTURE EQUIVALENT

In figure 6 the curves shown are similar to those in figure 5, the vertical ordinates in figure 6 being equivalent inches depth of water per foot depth of soil instead of soil moisture percentages as in figure 5. The general soil weights by which figure 5 is converted to figure 6 are shown at the top of the figure.

In addition the general soil types corresponding to the different values of the moisture equivalent have been written between figures 5 and 6 for convenience in reference.

In considering figures 3 to 6 the same statements regarding numerical accuracy will, of course, apply as were made regarding figures 1 and 2 from which they are derived. Caution should be used in applying figures 5 and 6, as further data will probably change the location of these curves. The general form of these curves is in agreement with general observations under field conditions and, in the author's opinion, they represent the nature of the relation of the moisture capacity of soils under field conditions to the soil texture. Further investigations might change the numerical values of points on such curves rather than their general form.

The form of the curves shown in figure 6 is in accord with general conditions of irrigation practice. Coarse soils, such as those having moisture equivalents of less than 10, are able to retain only limited amounts of water and consequently even where of good depth require frequent irrigations. In order to prevent excessive deep percolation losses on such soils the methods of irrigation must be adapted to covering them quickly so that the amount absorbed will not materially exceed the depth of water they are able to retain. On such types frequent irrigations are usually required, alfalfa generally receiving from two to three irrigations per cutting.

Soils having moisture equivalents of from 15 to 18 where of good depth are the most favorable of any in their moisture properties under irrigation. These combine a large moisture-storing capacity with a rate of absorption which permits them to be irrigated by such methods as will enable the moisture capacity to be utilized without excessive deep percolation losses. Such soils will usually carry alfalfa on one irrigation per cutting. Where properly handled very good economy in the utilization of irrigation supplies can be secured on these soils; where not properly prepared or where the water is not carefully handled they are sufficiently light to permit large percolation losses with consequent low efficiency in the application of water.

The heavy soils absorb water so slowly that it is usually not practicable to utilize the moisture capacity to the 5-foot depth without permitting the water to run sufficiently long so that other injuries such as scalding of the crop will occur. Frequently on such soils the moisture penetration will not exceed 2 feet in depth, with the result that frequent light applications must be made. This condition may cause a lower efficiency in the use of water and of the labor of its application than on soils of somewhat lighter texture.

The data presented, while subject to the limitations of extent and of accuracy covered in the above discussion, are thought to warrant the following general conclusions. All conclusions are limited in their application to field conditions under actual irrigation practice.

1. There is a fairly consistent relationship between the moisture equivalent and the various moisture properties of soils, which appears to offer promise of usefulness in determining moisture properties and probable irrigation practice of soils whose irrigation is contemplated, particularly as to the probable depth of water which will be retained from an irrigation with its effect on the depth to be applied and the necessary frequency of application.

2. The data presented, while indicating the general nature of the relationship of soil moisture capacity and soil texture, are not sufficient to fix the numerical values of such relationships except in a very general way.

3. The relationship of the soil-moisture properties to the moisture equivalent does not appear to be linear except in the case of the wilting of the crop.

4. The maximum depth of water per foot depth of soil which can be retained under favorable conditions for the upper 5 feet of soil is about 1.25 inches, which indicates that depths of single irrigation in excess of 6 to 8 inches, even under favorable soil conditions, will not be retained in the upper five or six feet of soil. This conclusion is in accord with the results of general field observations from many sources.

REFERENCE

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THE RELATION OF CERTAIN ACIDIC TO BASIC CONSTITUENTS OF THE SOIL AFFECTED BY AMMONIUM SULFATE AND NITRATE OF SODA[1]

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INTRODUCTION

It is well known that the continuous use of ammonium sulfate produces an acid condition in the soil, whereas nitrate of soda tends toward the production of an alkaline condition.

The former salt is referred to as a physiologically acid salt while the latter is physiologically alkaline. These two terms are significant phrases; the first indicates, for example, that ammonium sulfate is active in producing a condition in the soil which affects the plant from a physiological standpoint in much the same manner as does an acid.

An acid condition in soils is comparable to the condition of acidosis in the animal organism, and reflects a change in the position of equilibrium between acids and bases. A study of this relation of acids to bases should be of value in determining the cause of this acid condition resulting from the use of ammonium sulfate.

Perhaps the more reasonable theory has been that soil acidity resulting from the use of ammonium sulfate has been due to the relatively more extensive removal of the cation, which first undergoes nitrification, and then possible absorption by the plant. This leaves an excess of acid due to the sulfate radical; and, in case the NO_3 radical has not been removed by the plant, two acid radicals result.

These acid radicals react with bases, such as calcium and magnesium carbonates. These carbonates, which may be thought of as "buffer salts" or stabilizers of the soil reaction, may soon be inadequate to function in that capacity; they will have been neutralized by the sulfate or nitrate radical and the product either slowly leached away or retained in the soil as inactive constituents. This leaves the weaker bases, such as iron and aluminum, to act as preservers of neutrality of the soil solution. The salts of these are easily hydrolized and give rise to an acid condition. Inasmuch as the bases which are active in this reaction may be considered to be calcium, magnesium,

[1] Contribution No. 263 from the Agricultural Experiment Station of the Rhode Island State College.

iron and aluminum, these are the ones upon which most of this work is centered.

The literature on this subject has been reviewed so frequently that a repetition does not seem necessary. It appears more direct to present the experimental data secured, with such brief references to the literature as bear directly upon the problem.

SOILS

The soils on which this work was done were sampled in June, 1916, to the depth of 7 to 8 inches from permanent Rhode Island plats, which for the past twenty-five years have had like treatment, except that one series has been supplied with nitrogen in nitrate of soda while the other has received its supply in ammonium sulfate. The same comparison has existed with and without the addition of lime.

THE BASE AND ACID RETENTION OF THE SOIL

The "lime requirement" of these soils as indicated by the Veitch (12, p. 661) and ammonia (9) methods was as follows:

PLAT NUMBER	TREATMENT	CaO PER 2,000,000 POUNDS OF SOIL	
		Veitch method	Ammonia method
		lbs.	*lbs.*
23	Unlimed, $(NH_4)_2SO_4$	8,700	6,900
25	Limed, $(NH_4)_2SO_4$	5,800	5,200
27	Unlimed, $NaNO_3$	8,100	5,500
29	Limed, $NaNO_3$	4,800	3,700

References (5), (6), (7) and (8) of other papers from the Rhode Island Station will serve to extend the reader's acquaintance with the plats which are now again under consideration.

Although judging from the amount of ammonia retained by the soil from plat 29 after being brought to dryness over a hot-water bath, its lime requirement is 3700 pounds; yet a maximum growth of lettuce, a plant which is very sensitive to soil acidity, was obtained when the lime requirement had been reduced by liming only to 2800 pounds. It would appear, therefore, that for practical indications of the need for lime, too much ammonia was retained by the soil from plat 29. It is doubtful if any considerable amount was retained physically, for carbon black failed to exercise such retention under the conditions of the method.

The presence in the soil not only of acidic constituents but also of considerable amounts of basic iron and aluminum compounds suggested that the retention of acids might also be of importance. It was recognized that

these basic compounds are quite insoluble and inactive, and that if any combination were formed with a volatile acid, it would be quite unstable. No surprise was occasioned, therefore, when it was found that acetic acid was not retained under the following conditions: To 25 gm. of soil from plat 23 were added 75 cc. of normal acetic acid and the mixture digested at 35 to 40°C. for 1½ hours, after which distillation was carried out under reduced pressure at 82 to 90°C. until dryness was nearly attained, when 50 cc. of water was added and the process repeated.

When a non-volatile acid, however, was added the results were different, as shown by the following method: 10-gm. lots of soil were treated with 25, 50, 75 and 100 cc., respectively, of 0.2*N* H_3PO_4 and agitated for 70 hours. After this the solutions were made up to 200 cc., filtered off, and aliquots titrated with KOH and phenolphthalein. The maximum absorption by soils from plats 23 and 29 was found to be about alike and equivalent to 21,500 pounds of phosphoric oxide per 2,000,000 pounds of soil.

The foregoing demonstrates what a large basic effect the soil may exert under laboratory conditions. It must be recognized that even under certain natural conditions these basic compounds have some effect in counteracting acidic compounds, and to that extent any method of determining lime requirements which prevents the basic materials from exerting any effect is liable to overestimate the practical needs, as has already been shown to be the case with the growth of lettuce in relation to determinations of lime requirement by the use of ammonium hydroxide or calcium hydroxide, both of which substances would prevent all opportunity for the basic material in the soil to enter into the reaction.

It was shown by the following that a neutral salt may modify materially the lime requirements as determined by the ammonia method. A 0.07*N* solution with a pH of 7 by the Sörensen method was prepared by mixing mono- and di-ammonium phosphate. Before making the determination of lime requirements as usual by the ammonia method, 10 cc. of the phosphate solution were triturated lightly and occasionally with the soil by means of a pestle for an hour. The average depression in ammonia retention, caused by the addition of the ammonium phosphate, was 27 per cent, the variation with the four soils not being very marked. It is practically the mono-ammonium phosphate which is stable under the conditions of the method.

EXCHANGE OF BASES

One hundred and fifty grams of soil were shaken by inverting ten times at each interval of 15 minutes for a period of 3 hours with 500 cc. of a solution of normal KCl. These mixtures stood over night and were then filtered.

The reaction of the solutions was as follows:

Plat	
Unlimed, $(NH_4)_2SO_4$	Acid to methyl orange
Limed, $(NH_4)_2SO_4$	Slightly acid to methyl red
Unlimed, $NaNO_3$	Slightly acid to methyl red
Limed, $NaNO_3$	Neutral to neutral red

By titration of 50 cc. (equivalent to 15 gm. of soil) with phenolphthalein as indicator, the following was obtained:

PLAT	END POINT 0.01*N* NaOH	
	Cold	Hot
	cc.	*cc.*
Unlimed, $(NH_4)_2SO_4$	21.0	24.1
Limed, $(NH_4)_2SO_4$	2.3	3.0
Unlimed, $NaNO_3$	4.7	5.4
Limed, $NaNO_3$	0.6	0.8

During the titration of the extract from the unlimed sulfate of ammonia plat, a precipitate formed which resembled aluminum hydroxide. Ammonium hydroxide was added to an aliquot of the extract from each of the soils, but the precipitate formed only in the above-mentioned case. This precipitate was ignited and weighed. In an aliquot equivalent to 90 gm. of soil the weight of the precipitate was 0.0063 gm. If the acid condition revealed by titration with sodium hydroxide is attributed to the acidity of a hydrolyzed aluminum salt, and the weight of aluminum oxide is calculated equivalent to the sodium hydroxide used in the titration, we obtain, in an aliquot equivalent to 90 gm., a weight of 0.0066 gm. The weight obtained by direct precipitation and weighing was, as indicated above, 0.0063 gm. On this assumption practically all the titrated acidity may be accounted for as due to hydrolysis of an aluminum salt. G. Daikuhara (3) has demonstrated that in certain Japanese soils the acidity is proportional to the amount of aluminum present.

The analyses of the solutions follow:

Bases brought into solution from 90 gm. of soil by KCl

PLAT	Al_2O_3	CaO	MgO	TOTAL EXCHANGE OF BASES IN TERMS OF CaO
	gm.	*gm.*	*gm.*	*gm.*
Unlimed, $(NH_4)_2SO_4$	0.0063	0.0296	0.0026	0.0426
Limed, $(NH_4)_2SO_4$		0.0666	0.0113	0.0780
Unlimed, $NaNO_3$		0.0393	0.0028	0.0421
Limed, $NaNO_3$		0.1030	0.0187	0.1217

An exchange of base takes place when the four soils are treated with a solution of neutral potassium chloride. Potassium replaces calcium and magnesium from the limed plats while in the unlimed plat receiving ammonium sulfate, aluminum also is replaced. Considerable sulfur was present also in the latter instance. Ruprecht and Morse (11) report a similar exchange resulting from the use of ammonium sulfate.

EXTRACTION WITH 0.2 *N* HCl

Two hundred grams of soil were digested with 2 liters of 0.2*N* HCl at room temperature. The mixture was shaken by inverting ten times every hour for the first 8 hours. It was allowed to remain over night, filtered, and washed free of acid. The solution was evaporated, silicon hydroxide dehydrated, and the solution for analysis made in hydrochloric acid. The analysis of this solution follows:

PLAT	Al_2O_3 Fe_2O_3 P_2O_5 (TiO_2)	Fe_2O_3 — (TiO_2)	Al_2O_3	P_2O_5	CaO	MgO
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
Unlimed, $(NH_4)_2SO_4$	1.190	0.1515	0.9882	0.0503	0.0125	0.0009
Limed, $(NH_4)_2SO_4$	1.232	0.1224	1.0657	0.0439	0.0556	0.0057
Unlimed, $NaNO_3$	1.168	0.1120	1.0041	0.0519	0.0212	0.0021
*Limed, $NaNO_3$	1.229	0.0975	1.0805	0.0510	0.1091	0.0092

* This soil was the only one giving a reaction for manganese.

If it is true that a lack of calcium and magnesium imposes on iron and aluminum the responsibility of maintaining the neutrality of the soil solution, then on the unlimed as compared with the limed soil there should exist a very different relation between the two pairs of bases. This relation is shown by the following:

PLAT	$\frac{Al_2O_3 + Fe_2O_3}{CaO + MgO}$
Unlimed, $(NH_4)_2SO_4$	85.0
Limed, $(NH_4)_2SO_4$	19.4
Unlimed, $NaNO_3$	47.9
Limed, $NaNO_3$	10.0

A great variation does exist. It is impossible to estimate the actual significance of this relation but it harmonizes well with the belief that a great deal of the condition referred to as soil acidity is due to the hydrolysis of salts in which weak bases, such as iron and aluminum, are undertaking the responsibility preferably assumed by the stronger bases, calcium and magnesium.

EXTRACTION WITH NH_4OH

After the acid extraction, the soil was digested with 2 liters of 4 per cent NH_4OH by a procedure similar to that employed in making the acid extract. A clear solution was obtained by re-filtering several times through the soil mass on a large filter. The extract was boiled with ammonium carbonate and filtered. The following is the percentage analysis of this extract.

PLAT	Fe_2O_3	Al_2O_3	P_2O_5	CaO	MgO	SiO_2
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
Unlimed, $(NH_4)_2SO_4$	0.1366	0.0641	0.0857	0.0122	0.0007	0.0356
Limed, $(NH_4)_2SO_4$	0.1354	0.0900	0.0853	0.0086	0.0009	0.0321
Unlimed, $NaNO_3$	0.1571	0.1156	0.0984	0.0107	0.0009	0.0362
Limed, $NaNO_3$	0.1472	0.1356	0.0892	0.0142	0.0007	0.0435

In the analysis of this ammonia extract it appears that the per cent of phosphorus was not materially different on the several plats; this same observation holds true with silicon.

It is interesting to observe again the relation between the stronger and the weaker bases.

PLAT	$\frac{Fe_2O_3 + Al_2O_3}{CaO + MgO}$
Unlimed, $(NH_4)_2SO_4$	15.5
Limed, $(NH_4)_2SO_4$	23.7
Unlimed, $NaNO_3$	23.5
Limed, $NaNO_3$	18.9

The relations here do not show great variation as compared with those obtained from the acid extract. Only a small difference appears between the very acid soil and the nearly neutral soil. This would seem to indicate that the great difference existing in these soils is not to be attributed to an unsatisfactory relation of these bases in mainly organic combination but would indicate a disturbance in their relation in the inorganic system.

HYDROGEN ION CONCENTRATION

The hydrogen ion concentration in case of these soils has been measured by the colorimetric method[2] and found to be as follows:

[2] Essentially that employed by Gillespie (4) using the phthalate "buffer" mixtures (1, 2) and sulphonphthalein indicators.

PLAT	pH	(H')
Unlimed, $(NH_4)_2SO_4$	4.0	1×10^{-4}
Limed, $(NH_4)_2SO_4$	5.3	5×10^{-6}
Unlimed, $NaNO_3$	5.2	6.3×10^{-6}
Limed, $NaNO_3$	6.0	1×10^{-6}

It is seen that the concentration of hydrogen ions in these soils shows marked differences, ranging from an acidity of 0.0001*N* in the case of the unlimed ammonium sulfate plat to 0.000001*N* in the limed sodium nitrate plat, or a difference of a hundredfold in the intensity of reaction.

The concentration of hydrogen ions indicated by a pH of 4.0 with the unlimed sulfate of ammonia plat is a close approximation to the concentration of hydrogen ions which is developed by aluminum salts dissociating through a wide range of concentrations. If the same as the chloride, aluminum salts are about one-third dissociated (10); that is to say, in a solution of an aluminum salt, the acidity in terms of hydrogen ions is not the same as that developed by a mineral acid of the same normality, but is much less. Calculation of the acidity of an aluminum salt based upon titration is similar to that of a free acid since the hydrolysis of the salt proceeds with the titration.

The relation of acidity of $Al_2(SO_4)_3$ in terms of normality and of concentration of hydrogen ions is as follows:

NORMALITY	pH	(H')	NORMALITY IN TERMS OF (H')
0.100 *N*	3.4	4×10^{-4}	0.0004 *N*
0.010 *N*	3.7	2×10^{-4}	0.0002 *N*
0.001 *N*	4.0	1×10^{-4}	0.0001 *N*

In other words, a hundredfold increase in concentration based upon normality produces only a fourfold increase in concentration of hydrogen ions.

The concentration of hydrogen ions in the most acid soil is very close to that developed by these aluminum salts in solution, and experiment has shown that relatively large amounts of these salts can be added to a buffer solution without material change in the concentration of hydrogen ions; but the soil solution is a buffer solution containing phosphates and carbonates and so it appears that whatever the concentration of aluminum salts in the soil may be, they can never affect the concentration of hydrogen ions beyond a certain point, being held in check, as they are, first, by the dissociation constant; and second, by the buffer effect of phosphates and carbonates. This point of maximum concentration of hydrogen ions resulting from this equilibrium is believed to be expressed within narrow limits by a pH of 4.

SUMMARY

Great variation in acidity exists between soils receiving nitrogen in nitrate of soda as compared with those which receive it in sulfate of ammonia.

The soil, being a mixture in part of more or less inactive basic as well as acidic constituents, cannot have its "acidity" correctly measured by reagents which react only with the acidic ingredients.

Digestion with hydrochloric acid showed that great variation existed between the quotient obtained by dividing the oxides of aluminum and iron by those of calcium and magnesium. It ranged from 85 in the case of the unlimed soil receiving sulfate of ammonia to 10 where lime and nitrate of soda were employed.

A subsequent extract with ammonium hydroxide showed no great variation in this ratio of weak to strong bases.

An exchange of bases, produced by treatment of the soil with a solution of potassium chloride, showed a marked degree of reserve acidity from the unlimed soil receiving sulfate of ammonia. The acidity, so developed, showed a correlation to the acidity of an aluminum salt equivalent in amount to the weight of aluminum which was contained in the solution obtained by shaking with potassium chloride.

In the acid unlimed soils, iron and aluminum partially took the places occupied by calcium and magnesium in the limed soils.

The soil solution acts as a buffer solution containing phosphates and carbonates.

The concentration of hydrogen ions in the soil solution from the unlimed plat receiving sulfate of ammonia is very similar to that produced by the addition of even quite large amounts of aluminum salts to buffer solutions.

CONCLUSIONS

The "acidity" in a soil caused by long-continued use of ammonium sulfate is the result of a change in the ratio of acids to bases. The position normally occupied by the stronger bases, such as calcium and magnesium, has been taken by weaker bases, such as iron and aluminum. The neutrality of the soil solution can no longer be maintained since salts of these weak bases dissociate. Free acid resulting from this dissociation is accompanied by a definite concentration of hydrogen ions.

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CALCIUM AND MAGNESIUM CONTENT OF VIRGIN AND CULTIVATED SOILS

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INTRODUCTORY

The soil samples discussed in this paper were taken subsequent to the reconnoissance soil survey of Ohio, and although only a minority of the soil types of the state are represented by the samples which have been secured up to the present, the analytical work projected upon these has been completed and it seems desirable to make at least a partial report at this time. The relationships existing between total and fifth normal nitric acid soluble calcium and magnesium, carbonate content and reaction of the soil in those cases where both virgin and cultivated samples of the same soil type were taken in close proximity, have been considered.

SAMPLES STUDIED

Samples from the two depths 0 to 7 inches and 7 to 15 inches, designated "a" and "b," respectively, in the system of laboratory numbers, were prepared for analysis in the manner prescribed by the Association of Official Agricultural Chemists (3). The sampling was done under the supervision of E. R. Allen, formerly soil technologist at this station, to whom we are indebted for the description of individual soils, and for other aid.

ANALYTICAL METHODS

Total calcium and magnesium were determined by standard methods following a sodium peroxide fusion.

Fifth normal nitric-acid-soluble calcium and magnesium were determined in aliquots of a solution prepared by digesting 220 gm. of the air-dried and prepared sample with 2200 cc. of nitric acid of such strength that the acid in contact with the soil, after 5 hours' digestion at room temperature with shaking every half hour, should be exactly fifth normal as determined by titration of a boiled and cooled aliquot with standard sodium hydroxide and phenolphthalein in a preliminary experiment. At the end of the period prescribed, the solutions were filtered as rapidly as possible on large paper filters.

Carbonate was determined by the modified Marr method (3), titrating the residual barium hydroxide (5).

The qualitative tests for reaction were applied to the air-dried and prepared samples; Azolitmin (blue) and red litmus paper were doubled and pressed into a gash cut in a mass of the moistened soil and observed after one-half hour; the Veitch test was conducted exactly as originally described (8), save only that the extract was in every case filtered before being concentrated. The details of the Truog test were carefully followed as directed by the originator (7). All these tests were read as closely as possible, and in cases where the indications obtained were doubtful, the work was duplicated.

SIGNIFICANCE OF FIFTH NORMAL ACID SOLUBLE CALCIUM AND MAGNESIUM

In a former publication (2), the writers have presented data indicating that the fifth normal nitric acid soluble calcium and magnesium of the soil, exclusive of carbonates, approximates what may be termed the more active part of the soil's supply of the basic elements; in other words, the portion which is in combination with those constituents of the soil, whose residual capacity for absorption of a base (calcium) is indicated with more or less exactness by the term "lime requirement."

Shorey, Fry and Hazen (6) employed a method of leaching the soil with 2 per cent hydrochloric acid for the determination of that part of the soil's supply of calcium which may be present as calcium sulfate, calcium carbonate and in combination with humus; the calcium in the form of carbonate and sulfate can be calculated from other data, and any excess is supposed to represent calcium in combination with humus.

While it is doubtless a fact that a portion of the calcium and magnesium, other than carbonate, which is soluble in dilute acids is connected in some way with the organic matter of the soil, the writers are of the opinion that a more important part, in many soils, is present as very easily decomposable silicates or alumino-silicates, from which the bases are removed by acid much more dilute than 2 per cent hydrochloric acid. The data leading to this belief have been discussed (2).

It is certain that to assume all the calcium which is soluble in hydrochloric acid of 2 per cent or less strength, and not accounted for by the presence of carbonate or sulfate, to be in combination with organic matter will lead to unexpected results in some instances. An example which may be cited is the Spencer silt loam discussed by Shorey and his co-workers, the lower subsoil of which contains by far the largest percentage of calcium oxide with humus.

Data which would serve as a basis for an estimate of that part of the fifth normal nitric acid soluble calcium which is derived from calcium sulfate in the soils discussed in this paper are lacking. The omission is not considered very important, for the following reasons:

1. Shorey and associates in no case found any considerable quantity of calcium in the dilute acid extract which could be considered to be derived from calcium sulfate; the maximum amount was 0.02 per cent CaO on the basis of the sample, and in the majority of cases only a trace or none is reported.

2. The occurrence of any considerable amount of calcium sulfate in a normal soil of a humid region seems unlikely.

3. The neutralizing power of the soil was determined as a necessary preliminary to the fifth normal nitric acid digestion; the data thus obtained were also found useful as a check upon the accuracy of the calcium and magnesium determinations in the acid extracts.

Calcium sulfate could not affect the figures for acid consumed, therefore if the fifth normal nitric acid soluble calcium was appreciably in excess of the calcium equivalency of the acid neutralized, it could be attributed to calcium sulfate. Since no large difference was observed in this respect, it is evident that calcium sulfate was not present in sufficient amount to have any important bearing on the results.

DISCUSSION OF ANALYTICAL DATA

The analytical data for the soils studied are presented in table 1, and in addition to the contents of total and fifth normal nitric acid soluble calcium and magnesium, include data obtained from carbon-dioxide determinations, expressed as calcium carbonate content, and the reaction of the soils as determined by three well known qualitative tests. The percentages of the total calcium and magnesium contents soluble in fifth normal nitric acid are tabulated.

As a further aid to the interpretation of these analyses, the magnesium contents, both total and soluble, have been calculated to the equivalent amounts of calcium and these added to the corresponding figures for the calcium determined, calcium corresponding to the carbon dioxide found being deducted. As in the case of the two elements when considered separately, the percentages of the total amounts which are soluble have been tabulated.

The data last mentioned are considered to furnish useful information, as indicating both quantitatively and relatively the amount of the two bases together which may be considered as having combined with, and partially satisfied, the acid-reacting constituents. The bases present in the form of carbonates may be regarded as a reserve supply of the basic elements.

In a former publication from this laboratory (1), it was stated that for the Ohio soils studied it appeared to be a general rule that when total magnesium exceeds total calcium, no carbonates are present. With one or two exceptions, the rule appears to hold good for the soils discussed in this paper. A striking exception is the subsurface 33 b; here the amount of total magnesium is one and one-half times the percentage of total calcium, yet a very considerable quantity of carbonate is present. The proportion of the total mag-

nesium content of the soil soluble in 0.2*N* HNO_3 is unusually high, indicating that the carbonate in this soil is probably of dolomitic nature. It is noteworthy that the surface of the cultivated sample, number 32 b, taken near by, shows similar relations between total calcium and magnesium, and total and soluble magnesium, although in this case the soil is practically devoid of carbonate and reacts acid to tests. Samples 55 and 37 have much more total calcium than magnesium in both depths, but the presence of magnesium limestone is indicated by the considerable amount of magnesium soluble in 0.2*N* HNO_3.

The high amounts of magnesium found in the soils of western Ohio are doubtless due to the presence of a considerable amount of dolomitic limestone in the glacial till from which these soils are derived.

In table 2 is presented in compact form a summarized comparison of the analytical data for the virgin and cultivated samples analyzed. It will be observed that of the two elements, calcium is preponderant in the soil in the majority of cases, but that for approximately half of the samples magnesium exceeds calcium in the subsoil. In no case where the percentage of calcium in the subsoil is greater than the magnesium can this relation be attributed solely to the presence of carbonate of calcium.

Although but a comparatively small number of samples are represented, the two depths of cultivated and corresponding virgin soils exhibit some differences in their content of fifth normal nitric acid soluble calcium and magnesium, which appear to be of significance in showing changes which occur in soils as the result of cultivation.

In the majority of instances the proportion of total calcium and magnesium, calcium especially, soluble in fifth normal nitric acid, is greater in the surface virgin soil as compared with the same depth of cultivated soil. When the 7 to 15-inch depth of these soils is compared, the reverse of this is seen in many cases, the subsurfaces of the virgin sample containing less of these bases than the cultivated soil.

In contrasting the data for the individual cultivated and similar virgin soils as presented in table 1, it will be observed that the relations referred to are not uniform and consistent. This is to be expected in view of the differences which are to be found in the chemical composition of soils of the same type. Neither should too much significance be attached to small variations in composition. Attention has been directed to these points by Robinson, Steinkoenig and Fry (4).

Considering all the samples together, however, the averaged results should be fairly reliable in their indications of the effect of cultivation in promoting the action of natural solvent agencies, and in producing changes in the physical conditions, both of which affect the distribution of bases in different depths of soil.

Reaction and carbonate content

By far the greater number of samples examined show mere traces of carbonate; while this may possibly have been formed in some cases by the decomposition of organic matter during the analytical procedure, or may have been merely occluded by the soil, as suggested by Shorey and associates (6), the possibility of a local occurrence of carbonate in noncalcareous soils acid to tests should be considered. This condition could be attributed to isolated particles of carbonate minerals, or to plant residues containing organic salts of calcium which changed to carbonate during the process of decay.

There does not appear to be any consistent relation between carbonate content and reaction when the carbonate is present in very slight amount; some soils which are acid to the indicators employed contain as much carbonate as others strongly alkaline to tests, while one soil which was alkaline to the tests made, contains no carbonate at all. With larger amounts of carbonate —0.04 to 0.05 per cent—however, the reaction is always alkaline to litmus and the Veitch test, while the Truog test is usually negative or at most indicates "very slight acidity," except in one case (no. 33 b).

Another relationship which calls for comment is that between the amount of carbonate and the proportion of the non-carbonate calcium and magnesium soluble in 0.2*N* HNO_3. With but a single exception (again 33 b) in all cases where any considerable amount of carbonate is present, the proportion of the total calcium and magnesium not in the form of carbonate, but soluble in 0.2*N* HNO_3, is higher than in the sample from a different depth or taken nearby of the same type but containing less carbonate. Indeed, this connection is plainly seen in the great majority of cases where the calcium carbonate content is very low—0.01 to 0.02 per cent—and would seem to indicate that even these small figures for carbonate are not without significance, for they indicate basicity in other forms than carbonate.

In the greater number of instances, the indications of the three methods for determining the reaction of the soil are in agreement; the indications of the litmus and Veitch tests are occasionally at variance. These tests are not adapted to making comparisons as to degree of acidity or alkalinity of different soils, hence all soils which reddened blue litmus paper to a noticeable extent are called acid, while all whose water extracts were even slightly alkaline after concentration are considered alkaline by the Veitch test. In many cases where the indications are at variance, the soil was probably near the border line, as both tests were rather indistinct. The Truog test appears to indicate some acidity for many soils alkaline to the other tests.

In the case of some of the soil types under consideration, there appears to be a fairly consistent relation between the indications of the Truog test and the percentage of the total calcium and magnesium soluble in fifth normal nitric acid, exclusive of carbonates.

TABLE 1

Calcium and magnesium content and reaction of Ohio soils

DESCRIPTION		NUMBER	MAGNESIUM			CALCIUM			CALCIUM AND MAGNESIUM AS CALCIUM EXCLUSIVE OF CARBONATES			$CaCO_3$	REACTION		
			Total	0.2N HNO_3 soluble	Percentage of total soluble	Total	0.2N HNO_3 soluble	Percentage of total soluble	Total	0.2N HNO_3 soluble	Percentage of total soluble		Litmus	Truog	Veitch
			per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*			
Wooster loam	Cultivated	4a	0.236	0.0037	1.6	0.190	0.0360	19.0	0.576	0.0951	16.5	0.005	Acid	Medium acid	
		4b	0.269	0.0074	2.8	0.184	0.0561	30.5	0.627	0.0681	10.9		Acid	Strongly acid	
	Virgin	5a	0.210	0.0067	3.2	0.253	0.0900	35.6	0.591	0.093	15.7	0.020	Acid	Medium acid	
		5b	0.228	0.0081	3.6	0.148	0.0240	16.2	0.521	0.035	6.7	0.005	Acid	Strongly acid	
Wooster loam	Cultivated	6a	0.220	0.0054	2.5	0.223	0.0310	13.9	0.583	0.038	6.5	0.005	Acid	Medium acid	
		6b	0.250	0.0127	5.1	0.227	0.0413	18.2	0.638	0.062	9.7		Acid	Medium acid	
	Virgin	7a	0.258	0.0079	3.1	0.214	0.0410	19.2	0.638	0.054	8.5		Acid	Strongly acid	
		7b	0.261	0.0096	3.7	0.207	0.0478	23.1	0.625	0.053	8.5	0.028	Acid	Medium acid	
Wooster silt loam	Cultivated	8a	0.307	0.0100	3.3	0.312	0.0935	29.8	0.809	0.102	12.6	0.020	Acid	Slightly acid	
		8b	0.416	0.0180	4.3	0.283	0.0805	28.5	0.968	0.110	11.4		Acid	Strongly acid	
	Virgin	9a	0.288	0.0142	4.9	0.361	0.1638	45.3	0.816	0.168	20.6	0.048	Neutral	Very slightly acid	
		9b	0.276	0.0208	7.5	0.285	0.0588	20.6	0.737	0.091	12.3	0.005	Acid	Slightly acid	

Cincinnati silt loam	Cultivated	19a	0.256	0.0096	3.8	0.323	0.0922	28.5	0.742	0.106	14.3	0.005	Acid	Slightly acid	Alkaline
		19b	0.410	0.0164	4.0	0.270	0.1035	38.3	0.943	0.129	13.7	0.005	Acid	Medium acid	Alkaline
	Virgin	20a	0.274	0.0110	4.0	0.290	0.1151	39.7	0.735	0.128	17.4	0.013	Acid	Slightly acid	
		20b	0.315	0.0147	4.7	0.250	0.0667	26.7	0.768	0.091	11.9		Acid	Strongly acid	
Cincinnati silt loam	Cultivated	17a	0.262	0.0156	6.0	0.298	0.0981	32.9	0.720	0.115	16.0	0.023	Acid	Slightly acid	
		17b	0.332	0.0174	5.2	0.300	0.0812	27.1	0.845	0.108	12.8	0.005	Acid	Strongly acid	
	Virgin	23a	0.265	0.0091	3.6	0.250	0.0517	20.7	0.679	0.060	8.8	0.018	Acid	Slightly acid	
		23b	0.191	0.0180	9.4	0.210	0.0547	26.1	0.522	0.083	15.9	0.005	Acid	Very strongly acid	
Clermont silt loam	Cultivated	21a	0.256	0.0100	3.9	0.335	0.0881	26.3	0.754	0.103	13.7	0.005	Acid	Very slightly acid	Alkaline
		21b	0.287	0.0230	8.0	0.245	0.0818	33.4	0.715	0.118	16.5	0.005	Acid	Very strongly acid	
	Virgin	22a	0.238	0.0180	7.6	0.295	0.1065	36.1	0.681	0.131	19.2	0.015	Neutral	Very slightly acid	Alkaline
		22b	0.345	0.0240	7.0	0.285	0.0596	20.9	0.851	0.097	11.4	0.005	Acid	Very strongly acid	
Crosby silt loam	Cultivated	34a	0.269	0.0198	7.4	0.445	0.1343	30.2	0.887	0.167	18.8		Acid	Slightly acid	Alkaline
		34b	0.453	0.0442	9.8	0.430	0.0815	19.0	1.174	0.153	13.0	0.005	Acid	Very strongly acid	
	Virgin	35a	0.270	0.0257	9.5	0.440	0.0965	21.9	0.882	0.137	15.5	0.005	Acid	Medium acid	
		35b	0.416	0.0449	10.8	0.413	0.0640	15.5	1.096	0.136	12.4	0.005	Acid	Strongly acid	

TABLE 1—*Continued*

DESCRIPTION		NUMBER	MAGNESIUM			CALCIUM			CALCIUM AND MAGNESIUM AS CALCIUM EXCLUSIVE OF CARBONATES			$CaCO_3$	REACTION		
			Total	0.2*N* HNO_3 soluble	Percentage of total soluble	Total	0.2*N* HNO_3 soluble	Percentage of total soluble	Total	0.2*N* HNO_3 soluble	Percentage of total soluble		Litmus	Truog	Veitch
			per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*			
Lucas silt loam	Cultivated	38a	0.513	0.0355	6.9	0.593	0.1745	29.4	1.420	0.216	15.2	0.043	Alkaline	Slightly acid	Alkaline
		38b	0.789	0.0688	8.7	0.465	0.1560	33.6	1.761	0.267	15.2	0.005	Acid	Strongly acid	Alkaline
	Virgin	39a	0.553	0.0460	8.3	0.490	0.2240	45.7	1.392	0.292	21.0	0.020	Neutral	Very slightly acid	Alkaline
		39b	0.617	0.0548	8.9	0.538	0.2230	41.4	1.547	0.307	19.8	0.015	Neutral	Very slightly acid	Alkaline
Fox silt loam	Cultivated	59a	0.329	0.0200	6.1	0.415	0.1020	24.6	0.956	0.135	14.1		Acid	Medium acid	
		59b	0.449	0.0344	7.7	0.425	0.1493	35.1	1.163	0.206	17.7		Acid	Medium acid	Alkaline
	Virgin	60a	0.348	0.0385	11.1	0.498	0.1980	39.8	1.063	0.253	23.8	0.020	Neutral	Negative	Alkaline
		60b	0.496	0.0459	9.3	0.513	0.1900	37.0	1.325	0.262	19.8	0.010	Neutral	Very slightly acid	Alkaline
Maumee fine sand	Cultivated	28a	0.108	0.0029	2.7	0.320	0.0120	3.8	0.498	0.017	3.4		Acid	Very strongly acid	
		28b	0.108	0.0014	1.3	0.320	0.0027	0.8	0.498	0.005	1.0		Acid	Medium acid	
	Virgin	29a	0.200	0.0121	6.1	0.455	0.1250	27.5	0.784	0.145	18.5		Acid	Slightly acid	
		29b	0.126	0.0064	5.1	0.420	0.0790	18.8	0.627	0.090	14.4		Acid	Slightly acid	

Newton loam	Cultivated	49a	0.510	0.0594	11.7	1.035	0.4975	48.1	1.870	0.592	31.7	0.010	Alkaline	Negative	Alkaline
		49b	0.478	0.0677	14.2	0.828	0.3831	46.3	1.613	0.492	30.5	0.005	Alkaline	Negative	Alkaline
	Virgin	50a	0.422	0.0635	15.1	1.130	0.5174	45.8	1.804	0.600	33.3	0.054	Alkaline	Negative	Alkaline
		50b	0.409	0.0645	15.8	0.870	0.3632	41.8	1.537	0.463	30.2	0.015	Alkaline	Negative	Alkaline
Dunkirk fine sand	Cultivated	25a	0.240	0.0085	3.5	0.620	0.0508	8.2	1.015	0.065	6.4	0.005	Neutral	Slightly acid	Alkaline
		25b	0.205	0.0027	1.3	0.485	0.0162	3.3	0.822	0.021	2.5		Neutral	Medium acid	
	Virgin	26a	0.183	0.0069	3.8	0.435	0.0359	8.3	0.736	0.047	6.4		Acid	Medium acid	
		26b	0.170	0.0034	2.0	0.430	0.0050	1.2	0.710	0.011	1.5		Acid	Medium acid	
Dunkirk fine sand	Cultivated	45a	0.223	0.0048	2.2	0.555	0.0400	7.2	0.921	0.048	5.2		Alkaline	Very slightly acid	Alkaline
		45b	0.244	0.0029	1.2	0.540	0.0195	3.6	0.941	0.024	2.6		Alkaline	Very slightly acid	Alkaline
	Virgin	46a	0.253	0.0039	1.5	0.590	0.0215	3.6	1.006	0.028	2.8		Acid	Medium acid	
		46b	0.286	0.0034	1.2	0.663	0.0160	2.4	1.133	0.022	1.9		Acid	Slightly acid	
Dunkirk fine sand	Cultivated	47a	0.198	0.0123	6.2	0.575	0.0610	10.6	0.871	0.051	5.9	0.074	Alkaline	Negative	Alkaline
		47b	0.228	0.0044	1.9	0.690	0.0265	3.8	1.059	0.033	3.1	0.015	Alkaline	Negative	Alkaline
	Virgin	48a	0.202	0.0086	4.3	0.585	0.0194	3.3	0.917	0.034	3.7		Acid	Very strongly acid	
		48b	0.263	0.0055	2.1	0.533	0.0194	3.6	0.966	0.028	2.9		Acid	Very strongly acid	
Belmore sandy loam	Cultivated	55a	0.286	0.0893	31.2	0.890	0.4149	46.7	1.136	0.337	29.7	0.561	Alkaline	Negative	Alkaline
		55b	0.301	0.0298	9.9	0.685	0.2507	36.6	1.117	0.241	21.5	0.149	Alkaline	Negative	Alkaline
	Virgin	56a	0.242	0.0183	7.6	0.593	0.1781	30.1	0.985	0.202	20.5	0.015	Alkaline	Negative	Alkaline
		56b	0.268	0.0181	6.8	0.520	0.1493	28.7	0.865	0.173	17.9	0.015	Alkaline	Very slightly acid	Alkaline

TABLE 1—*Continued*

DESCRIPTION		NUMBER	MAGNESIUM			CALCIUM			CALCIUM AND MAGNESIUM AS CALCIUM EXCLUSIVE OF CARBONATES			$CaCO_3$	REACTION		
			Total	0.2*N* HNO_3 soluble	Percentage of total soluble	Total	0.2*N* HNO_3 soluble	Percentage of total soluble	Total	0.2*N* HNO_3 soluble	Percentage of total soluble		Litmus	Truog	Veitch
			per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*			
Miami silty clay loam	Cultivated	30a	0.722	0.0290	4.0	0.393	0.1123	28.6	1.578	0.158	10.0	0.005	Acid	Medium acid	
		30b	0.682	0.0681	10.0	0.373	0.1555	41.7	1.493	0.266	17.8	0.005	Acid	Very strongly acid	
	Virgin	31a	0.372	0.0229	6.2	0.480	0.2204	45.9	1.079	0.245	22.7	0.033	Alkaline	Slightly acid	Alkaline
		31b	0.569	0.0351	6.2	0.280	0.0790	28.2	1.213	0.133	11.0	0.010	Acid	Very strongly acid	
Miami silty clay loam	Cultivated	32a	0.381	0.0269	7.1	0.390	0.1113	28.6	1.008	0.146	14.5	0.023	Acid	Medium acid	Alkaline
		32b	0.553	0.0892	15.6	0.360	0.1689	46.9	1.259	0.304	24.2	0.030	Acid	Medium acid	
	Virgin	33a	0.335	0.0298	8.9	0.475	0.1816	38.2	1.022	0.226	22.1	0.013	Acid	Medium acid	
		33b	0.730	0.1623	22.3	0.525	0.3089	58.8	1.441	0.291	20.2	0.713	Alkaline	Slightly acid	Alkaline
Brookston silty clay loam	Cultivated	36a	0.583	0.0772	13.2	0.810	0.3680	45.4	1.766	0.491	27.8	0.010	Alkaline	Very slightly acid	Alkaline
		36b	0.688	0.0984	14.3	0.840	0.3570	42.5	1.966	0.516	26.3	0.015	Alkaline	Negative	Alkaline
	Virgin	37a	0.645	0.1490	23.1	1.040	0.6160	59.2	2.040	0.799	39.2	0.155	Alkaline	Negative	Alkaline
		37b	0.768	0.2051	26.7	0.985	0.5640	57.2	2.000	0.654	32.7	0.621	Alkaline	Negative	Alkaline

Brookston clay loam	Cultivated	40a	0.471	0.0428	9.1	1.145	0.4950	43.2	1.909	0.553	29.0	0.030	Alkaline	Negative	Alkaline
		40b	0.568	0.0528	9.3	0.888	0.3700	41.6	1.815	0.449	24.8	0.020	Alkaline	Negative	Alkaline
	Virgin	41a	0.549	0.0579	10.5	1.280	0.6380	49.9	2.161	0.711	32.9	0.056	Alkaline	Negative	Alkaline
		41b	0.627	0.0560	8.9	0.918	0.3500	38.1	1.940	0.432	22.3	0.025	Alkaline	Negative	Alkaline
Brookston clay	Cultivated	42a	0.420	0.0298	7.1	0.708	0.2687	37.9	1.393	0.312	22.5	0.015	Neutral	Very slightly acid	Alkaline
		42b	0.642	0.0709	11.0	0.635	0.2520	39.7	1.687	0.365	21.7	0.010	Alkaline	Very slightly acid	Alkaline
	Virgin	43a	0.636	0.0872	13.7	1.095	0.6840	62.5	1.972	0.659	33.4	0.422	Alkaline	Negative	Alkaline
		43b	0.631	0.0660	10.5	0.820	0.3950	48.2	1.853	0.499	27.0	0.013	Alkaline	Negative	Alkaline
Brookston clay	Cultivated	51a	0.694	0.0724	10.4	1.135	0.6079	52.6	2.267	0.717	31.6	0.025	Alkaline	Negative	Alkaline
		51b	0.774	0.0994	12.2	1.060	0.6288	59.3	2.114	0.572	27.1	0.549	Alkaline	Negative	Alkaline
	Virgin	52a	0.693	0.0919	13.3	1.160	0.6865	59.2	2.243	0.780	34.8	0.144	Alkaline	Negative	Alkaline
		52b	0.792	0.0922	11.7	0.975	0.4925	50.5	2.267	0.633	28.0	0.028	Alkaline	Negative	Alkaline
Newton silty clay	Cultivated	53a	0.675	0.0896	13.3	1.280	0.8822	68.9	2.276	0.926	40.7	0.260	Alkaline	Negative	Alkaline
		53b	0.769	0.0927	12.1	0.895	0.5104	57.0	2.149	0.651	30.3	0.030	Alkaline	Negative	Alkaline
	Virgin	54a	0.729	0.0853	11.7	1.180	0.7721	65.5	2.372	0.904	38.1	0.020	Alkaline	Negative	Alkaline
		54b	0.848	0.0589	6.9	0.925	0.5055	54.7	2.316	0.598	25.9	0.013	Alkaline	Negative	Alkaline
Brookston clay	Cultivated	57a	0.826	0.0773	9.4	1.025	0.5791	56.5	2.380	0.702	29.5	0.010	Alkaline	Very slightly acid	Alkaline
		57b	0.819	0.0890	10.9	0.858	0.4497	52.4	2.200	0.590	26.8	0.015	Alkaline	Negative	Alkaline
	Virgin	58a	0.697	0.0942	13.5	1.125	0.7323	65.1	2.250	0.865	38.5	0.554	Alkaline	Negative	Alkaline
		58b	0.785	0.0879	11.2	0.820	0.4428	54.0	2.104	0.580	27.6	0.020	Alkaline	Negative	Alkaline

TABLE 2

Cultivated and virgin samples of the same soil types compared

	CULTIVATED	VIRGIN
	per cent	*per cent*
Total calcium in soil exceeds total magnesium in soil	91	87
Total calcium in subsoil exceeds total magnesium in subsoil	48	61
Total magnesium in subsoil is greater than total magnesium in surface soil	78	74
0.2*N* HNO_3 soluble magnesium in subsoil is greater than 0.2*N* HNO_3 soluble magnesium in soil	83	61
Percentage of total magnesium soluble is greater in subsoil than in soil	70	48
Total calcium in soil is greater than in subsoil	74	83
0.2*N* HNO_3 soluble calcium is greater in soil than in subsoil	70	83
Percentage of total calcium soluble is greater in soil than in subsoil	57	83
Percentage of both bases soluble, exclusive of carbonates, is greater in soil than in subsoil	74	91

* Per cent of cases in 23 samples.

SUMMARY

In this paper, the contents of total and fifth normal nitric acid soluble calcium and magnesium, carbonate and reaction of both virgin and cultivated soils from 23 locations in Ohio are discussed.

The data indicate that in most virgin soils there is a concentration of readily soluble calcium and magnesium at the surface. With cultivated soils, however, the subsoil is usually better supplied with these elements than the surface soil.

Certain interesting relationships between the proportion of the total calcium and magnesium which are soluble, and carbonate content and reaction are pointed out. These may be summarized in the statement that when the proportion of the total bases (calcium and magnesium together) which is soluble, is high, the soil is very likely to contain more carbonate or to be more basic to tests than is the case with similar soils having a less proportion of these bases soluble. Moreover, this is true for soils containing very small amounts, as well as those better supplied with carbonates.

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